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# Equilibrium Constants of Some Reactions Involved in the Production of 1,3-Butadiene[1]

*By Ferdinand G. Brickwedde, Morris Moskow, and John G. Aston*[2]

Thermodynamic functions including free energy, enthalpy, entropy, and specific heat, are given for the compounds butadiene, benzene, cyclohexane, ethane, ethylene, ethyl alcohol and water and for the elements carbon (graphite), hydrogen and oxygen. From these are calculated and tabulated values of equilibrium constants for reactions of interest in connection with the production of 1,3-butadiene for synthetic rubber. Comparisons are made between table values and available experimental data on equilibrium constants, gaseous specific heats and entropies. The cracking of hydrocarbons is discussed and the importance of reaction rates in determining the amounts of reaction products is noted.

## I. Introduction

In an earlier publication the measured thermal properties of 1,3-butadiene including heat capacities down to 15° K were used to determine the entropy and enthalpy of butadiene to 300° K [1, 2].[3] With these calorimetric data and the most recent spectroscopic data, the thermodynamic functions for butadiene were then extended to higher temperatures. These were combined with the thermodynamic functions for *n*-butane and the *n*-butenes to calculate the equilibrium constants for the dehydrogenation reactions of *n*-butane and *n*-butenes used in the manufacture of butadiene from petroleum and natural gas. [3, 4].

In the present paper are given values for thermodynamic functions and properties of a number of other compounds for use in calculations of equilibria occurring in other reactions involved in the commercial production of 1,3-butadiene for synthetic rubber. These compounds are benzene, cyclohexane, ethane, ethylene, ethyl alcohol, and water. Tables for the elements graphite, hydrogen, and oxygen also have been included. Tables

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[1] This paper is a revision of a report entitled, "Equilibrium constants of some reactions involved in the production of 1,3-butadiene," submitted to the Office of the Rubber Director, March 24, 1944.
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[3] Figures in brackets indicate literature references at the end of this paper.

of equilibrium constants are given for the following reactions:

$C_6H_8+3H_2 \rightleftharpoons C_6H_{12}$ (cyclohexane).

$C_6H_{12}$ (cyclohexane) $\rightleftharpoons C_4H_6$ (1,3-butadiene) $+C_2H_4+H_2$.

$C_6H_{12}$ (cyclohexane) $\rightleftharpoons C_4H_6$ (1,3-butadiene) $+C_2H_6$.

$C_6H_{12}$ (cyclohexane) $\rightleftharpoons C_4H_6$ (1,3-butadiene) $+C_2H_2+2H_2$.

$C_6H_{12}$ (cyclohexane) $\rightleftharpoons 3/2\ C_4H_6$ (1,3-butadiene) $+3/2\ H_2$.

$C_6H_{12}$ (cyclohexane) $\rightleftharpoons 3C_2H_4$.

$2C_2H_4 \rightleftharpoons C_4H_6$ (1,3-butadiene) $+H_2$.

$2C_2H_4 \rightleftharpoons n$-$C_4H_8$ (1-butene, *cis* and *trans*-2-butene, and mixture).

$C_2H_6 \rightleftharpoons C_2H_4+H_2$.

$2C_2H_5OH \rightleftharpoons C_4H_6$ (1,3-butadiene) $+2H_2O+H_2$.

$C_2H_4+H_2O \rightleftharpoons C_2H_5OH$.

$C_2H_4+C_2H_2 \rightleftharpoons C_4H_6$ (1,3-butadiene).

$C_2H_4 \rightleftharpoons C_2H_2+H_2$.

$C_2H_6 \rightleftharpoons C_2H_2+2H_2$.

$C_2H_4+C_4H_6$ (1,3-butadiene) $\rightleftharpoons C_6H_8$ (g) $+2H_2$.

$2C_4H_6$ (1,3-butadiene) $\rightleftharpoons C_6H_8$ (g) $+C_2H_4+H_2$.

The thermodynamic functions and properties of all the substances included in this paper, with the exception of cyclohexane, have been previously calculated and published by others. However new values for these functions and properties have been calculated for this paper, taking account the latest spectroscopic and calorimetric data by using the latest values of the fundamental physical constants.[4] In a number of cases, the frequency assignments adopted cannot be regarded as certain but appear to be the most reasonable that have been proposed. It is thought that, in general, further improvements in the values taken for the fundamental frequencies given in this paper would result in only small changes of the calculated thermodynamic properties.

The thermodynamic functions and properties are given in tables 1 to 24.[5] Data and calculations upon which these tables are based are discussed in sections II to XI. Comparisons between calculated and experimental entropies and heat capacities are included for most of the compounds. The heats of formation of the compounds are discussed in section XII. The equilibrium constants of the reactions are given in tables 25 to 29 and are discussed in section XIII. In section XIV the results of some investigations on cracking reactions are compared with theoretically predicted equilibrium concentrations.

[4] The physical constants include $hc/k=1.4384$ cm deg, $R=1.98714$ [illegible] cal deg$^{-1}$ mole$^{-1}$ or $8.3144\times10^7$ erg deg$^{-1}$ mole$^{-1}$, and $N_0=6.0228\times10^{23}$ [illegible] with 1 artificial calorie defined as 4.1833 international joules. The atomic weights used are hydrogen 1.0080, carbon 12.01, and oxygen 16.

[5] In these tables the following conventions have been adopted: For entropy, $H°$, and for free energy, $F°$, the quantities are given as values above assumed zeros for the elements in their standard states at 0° K. $\Delta H°$, $\Delta F°$ and $K$, respectively, are the enthalpy of formation, the free energy of formation, and the equilibrium constant of formation of the compound from the elements in their standard states at the temperature $T$.

## II. Butadiene

Thermodynamic functions for 1,3-butadiene from reference [4] are given in tables 1 and 2. As indicated in that publication, it is concluded that 1,3-butadiene has more than one form, since, for any vibration assignment that seemed reasonable, the specific heat calculated did not agree with the experimental when it was assumed that only a single form existed. Agreement with the experimental calorimetric data was obtained by the use of a *cis* and a *trans* form.

Except for the frequency of torsion about the central C—C bond, the distribution of energy levels has been assumed to be statistically the same for the *cis* as for the *trans* variety. The frequency assignment for the *trans* variety is mainly that of Bradacs and Kahovec [5]. It differs in the following. The observed Raman line 340 cm$^{-1}$ that Bradacs and Kohovec assigned with expressed doubt, to the fundamental of the middle C—C torsional vibration was assigned by us to the first overtone of this vibration. For double-bond torsions the observed 520 cm$^{-1}$ and a calculated 667 cm$^{-1}$ based on ethylene have been used. For the skeletal deformation frequency the 520 cm$^{-1}$ used by Bradacs and Kahovec has been replaced by 326 cm$^{-1}$ on the basis of force constant calculations and the calorimetric data. The barrier heights are 5,000 cal mole$^{-1}$ for the *trans* form and 2,575 cal mole$^{-1}$ for the *cis* form.

TABLE 1.—*Heat capacity at constant pressure, heat content, and related quantities of 1,3-butadiene in the ideal gas state*

[$E^\circ_0$=30,200 cal mole$^{-1}$]

| $T$ | $\frac{H^\circ-E^\circ_0}{T}$ | $H^\circ$ | $^a\Delta H^\circ$ | $C^\circ_p$ |
|---|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ | cal mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ |
| 298.16 | 12.16 | 33,830 | 26,750 | 19.01 |
| 300.00 | 12.20 | 33,860 | 26,730 | 19.11 |
| 400 | 14.59 | 36,040 | 25,830 | 24.29 |
| 500 | 16.97 | 38,690 | 25,120 | 28.52 |
| 600 | 19.18 | 41,710 | 24,540 | 31.84 |
| 700 | 21.19 | 45,040 | 24,080 | 34.55 |
| 800 | 23.01 | 48,610 | 23,710 | 36.84 |
| 900 | 24.66 | 52,390 | 23,420 | 38.81 |
| 1,000 | 26.16 | 56,360 | 23,210 | 40.52 |
| 1,100 | 27.54 | 60,490 | 23,060 | 42.02 |
| 1,200 | 28.80 | 64,760 | 22,980 | 43.32 |
| 1,300 | 29.96 | 69,150 | 22,940 | 44.47 |
| 1,400 | 31.03 | 73,650 | 22,950 | 45.47 |
| 1,500 | 32.02 | 78,240 | 22,980 | 46.34 |

$^aH^\circ$ is the enthalpy of formation of 1,3-butadiene from its elements in their standard states at the temperature $T$.

TABLE 2.—*Entropy, free energy, and related quantities of 1,3-butadiene in the ideal gas state at 1-atmosphere pressure*

[$E^\circ_0$=30,200 cal mole$^{-1}$]

| $T$ | $-\left(\frac{F^\circ-E^\circ_0}{T}\right)$ | $S^\circ$ | $-F^\circ$ | $^a\Delta F^\circ$ | $^a\log_{10}K$ |
|---|---|---|---|---|---|
| | | | | | $-\Delta F^\circ/RT$ |
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ | cal mole$^{-1}$ | 2.3026 |
| 298.16 | 54.46 | 66.62 | −13,960 | 36,430 | −26.707 |
| 300.00 | 54.54 | 66.74 | −13,840 | 36,490 | −26.587 |
| 400 | 58.28 | 72.97 | −6,850 | 39,890 | −21.793 |
| 500 | 61.89 | 78.86 | +740 | 43,490 | −19.009 |
| 600 | 65.18 | 84.36 | 8,920 | 47,210 | −17.198 |
| 700 | 68.29 | 89.48 | 17,600 | 51,040 | −15.934 |
| 800 | 71.24 | 94.25 | 26,790 | 54,920 | −15.003 |
| 900 | 74.05 | 98.71 | 36,440 | 58,830 | −14.287 |
| 1,000 | 76.72 | 102.88 | 46,520 | 62,780 | −13.721 |
| 1,100 | 79.28 | 106.82 | 57,010 | 66,740 | −13.260 |
| 1,200 | 81.73 | 110.53 | 67,880 | 70,720 | −12.880 |
| 1,300 | 84.09 | 114.05 | 79,110 | 74,690 | −12.557 |
| 1,400 | 86.35 | 117.38 | 90,680 | 78,670 | −12.281 |
| 1,500 | 88.52 | 120.54 | 102,580 | 82,660 | −12.043 |

$^a\Delta F^\circ$ and $K$ are the free-energy change and equilibrium constant, respectively, for the reaction forming 1, 3-butadiene from its elements in their standard states at $T$°K.

# III. Benzene

The frequencies assigned to the fundamental modes of vibration of the benzene molecule by K. S. Pitzer and D. W. Scott were used for this paper [6]. These frequencies in centimeters$^{-1}$ are as follows:

*Carbon skeleton frequencies:*

Vibrations in the plane of the molecule: $\omega_1=\omega_2=606$, $\omega_3=1011$, $\omega_4=992$, $\omega_5=\omega_6=1485$, $\omega_7=\omega_8=1596$, and $\omega_9=(1693)$.

Vibrations out of the plane of the molecule: $\omega_{10}=(685)$ and $\gamma_2=\gamma_3=400$.

*Frequencies due to* CH *groups:*

$\gamma$(CH) waving motions out of the plane of the molecule: (1016), 849(2), 671, and (985)(2).

$\delta$(CH) waving motions in the plane of the molecule: (1298), 1178(2), (1170), and 1037(2).

$\nu$(CH) stretching motions: 3062, 3047(2), 3046, and 3080(2). The frequencies in parentheses have not been observed because the vibrations to which they correspond are optically inactive. The benzene molecule is planar, a regular hexagon with distances between carbon atoms equal to 1.39 A and distances between carbon and hydrogen atoms of 1.09 A. The symmetry number is 12. The principal moments of inertia about the center of mass are $292.9\times10^{-40}$ g cm$^2$, $146.5\times10^{-40}$ g cm$^2$, and $146.5\times10^{-40}$ g cm$^2$. Their product is $6.28\times10^{-114}$ g$^3$ cm$^6$.

Calculated values of thermodynamic functions and properties are given in tables 3 and 4. The moderate departures of calculated values of $-(F^\circ-E^\circ_0)/T$, $H^\circ-E^\circ_0$, and $C^\circ_p$ from those of reference [6] are thought to be due to the use of the latest values for the fundamental physical constants in the present calculations. The source of the value for $E^\circ_0$ used in this paper is given in section XII.

Table values of $C^\circ_p$ are in agreement to within experimental accuracy with values of $C^\circ_p$ derived from the calorimetrically measured heat capacities, which extend over the range 360° to 480°K. This may be seen in figure 7 in the paper by Pitzer and Scott, since the sets of calculated values of $C^\circ_p$ in the two papers are in agreement to within less than the experimental error.

TABLE 3.—*Heat capacity at constant pressure, heat content, and related quantities of benzene in the ideal gas state*

[$E_0^\circ$=24,000 cal mole$^{-1}$]

| $T$ | $\frac{H^\circ - E_0^\circ}{T}$ | $H^\circ$ | $^a\Delta H^\circ$ | $C_p^\circ$ |
|---|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ | cal mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ |
| 298.16 | 11.41 | 27,400 | 19,820 | 19.51 |
| 300.00 | 11.46 | 27,440 | 19,800 | 19.65 |
| 400 | 14.41 | 29,760 | 18,550 | 26.74 |
| 500 | 17.50 | 32,750 | 17,540 | 32.80 |
| 600 | 20.48 | 36,290 | 16,720 | 37.74 |
| 700 | 23.24 | 40,270 | 16,070 | 41.75 |
| 800 | 25.76 | 44,610 | 15,570 | 45.06 |
| 900 | 28.07 | 49,260 | 15,170 | 47.82 |
| 1,000 | 30.16 | 54,160 | 14,880 | 50.16 |
| 1,100 | 32.07 | 59,280 | 14,680 | 52.15 |
| 1,200 | 33.82 | 64,580 | 14,550 | 53.85 |
| 1,300 | 35.42 | 70,040 | 14,490 | 55.31 |
| 1,400 | 36.88 | 75,640 | 14,490 | 56.57 |
| 1,500 | 38.23 | 81,350 | 14,500 | 57.66 |

[a] $\Delta H^\circ$ is the enthalpy of formation of benzene from its elements in their standard states at the temperature $T$.

TABLE 4.—*Entropy, free energy and related quantities of benzene in the ideal gas state at 1-atmosphere pressure*

[$E_0^\circ$=24,000 cal mole$^{-1}$]

| $T$ | $-\left(\frac{F^\circ - E_0^\circ}{T}\right)$ | $S^\circ$ | $-F^\circ$ | $^a\Delta F^\circ$ | $^a\log_{10} K$ |
|---|---|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ | cal mole$^{-1}$ | $-\Delta F^\circ/RT$ |
| 298.16 | 52.94 | 64.34 | −8,220 | 31,000 | 22.728 |
| 300.00 | 53.01 | 64.46 | −8,100 | 31,070 | 22.694 |
| 400 | 56.70 | 71.10 | −1,320 | 35,020 | 19.133 |
| 500 | 60.25 | 77.74 | +6,120 | 39,260 | 17.161 |
| 600 | 63.70 | 84.18 | 14,220 | 43,680 | 15.910 |
| 700 | 67.07 | 90.31 | 22,950 | 48,230 | 15.024 |
| 800 | 70.34 | 96.10 | 32,270 | 52,860 | 14.402 |
| 900 | 73.51 | 101.57 | 42,160 | 57,550 | 13.972 |
| 1,000 | 76.58 | 106.74 | 52,580 | 62,270 | 13.610 |
| 1,100 | 79.54 | 111.61 | 63,490 | 67,020 | 13.315 |
| 1,200 | 82.41 | 116.23 | 74,890 | 71,790 | 13.078 |
| 1,300 | 85.18 | 120.60 | 86,730 | 76,550 | 12.880 |
| 1,400 | 87.86 | 124.74 | 99,000 | 81,320 | 12.708 |
| 1,500 | 90.45 | 128.68 | 111,670 | 86,100 | 12.560 |

[a] $\Delta F^\circ$ and $K$ are the free-energy change and equilibrium constant, respectively, for the reaction forming benzene from its elements in their standard states at $T$ °K.

# IV. Cyclohexane

The frequency assignment used in the calculations for cyclohexane is essentially the same as one given previously [7]. A value of 673 cm$^{-1}$, which was used in a previous form of this paper for one frequency, has now been replaced by 864 cm$^{-1}$ on the ground that the band reported at 673 cm$^{-1}$ was due to an impurity.[6] The molecule has a chair form with $D_{3d}$ symmetry, for which the symmetry number is 6. The frequencies in cm$^{-1}$ used were as follows:

*Carbon skeleton frequencies:*

Vibrations essentially parallel to the $\sigma_s$ plane: $\omega_1 = \omega_2 = 425$, $\omega_3 = 864$, $\omega_4 = 801$, $\omega_5 = \omega_6 = 1050$, $\omega_7 = \omega_8 = 1266$, and $\omega_9 = 1370$.

Vibrations essentially parallel to the principal axis [$C_3$] of the molecule: $\gamma_1 = \gamma_2 = 196$ and $\gamma_3 = 377$.

*Frequencies due to* $CH_2$ *groups:*

$\gamma(CH_2)$ waving motions: 885(6), 1028(6), and 1345(6).

$\delta$(HCH) bending motions: 1300(6).

$\nu$(CH) stretching motions: 2770(12).

The frequency of the optically inactive, and doubly degenerate, rocking motion of the carbon skeleton, $\gamma_1 = \gamma_2$, was calculated from the calorimetrically determined entropy [8] by using the assignments given here for the remaining frequencies.

The distance between carbon atoms was taken as 1.54 A and between carbon and hydrogen atoms as 1.09 A. Using tetrahedral angles, the principal moments of inertia are $335.1 \times 10^{-40}$ g cm$^2$, $193.8 \times 10^{-40}$ g cm$^2$, and $193.8 \times 10^{-40}$ g cm$^2$, giving for the product of the three $12.58 \times 10^{-114}$ g$^3$ cm$^6$.

Tables 5 and 6 give the calculated values

TABLE 5.—*Heat capacity and constant pressure, heat content, and related quantities of cyclohexane in the ideal state*

[$E_0^\circ$=19,950 cal mole$^{-1}$]

| $T$ | $\frac{H^\circ - E_0^\circ}{T}$ | $H^\circ$ | $^a\Delta H^\circ$ | $C_p^\circ$ |
|---|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ | cal mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ |
| 298.16 | 14.13 | −15,740 | −29,380 | 25.15 |
| 300.00 | 14.20 | −15,690 | −29,440 | 25.35 |
| 400 | 18.31 | −12,630 | −32,030 | 35.87 |
| 500 | 22.80 | −8,550 | −34,050 | 45.42 |
| 600 | 27.26 | −3,590 | −35,550 | 53.49 |
| 700 | 31.50 | +2,100 | −36,590 | 60.15 |
| 800 | 35.44 | 8,400 | −37,260 | 65.77 |
| 900 | 39.08 | 15,220 | −37,610 | 70.50 |
| 1,000 | 42.43 | 22,480 | −37,700 | 74.51 |
| 1,100 | 45.50 | 30,100 | −37,580 | 77.93 |
| 1,200 | 48.33 | 38,040 | −37,270 | 80.82 |
| 1,300 | 50.93 | 46,250 | −36,820 | 83.30 |
| 1,400 | 53.31 | 54,690 | −36,250 | 85.42 |
| 1,500 | 55.52 | 63,330 | −35,610 | 87.20 |

[a] $\Delta H^\circ$ is the enthalpy of formation of cyclohexane from its elements their standard states at the temperature $T$.

[6] A private communication from E. K. Plyler, of the Radiometry Section of the National Bureau of Standards, indicates that there is no evidence for a band at 673 cm$^{-1}$ when a very pure sample of cyclohexane is used.

TABLE 6.—*Entropy, free energy, and related quantities of cyclohexane in the ideal gas state at 1-atmosphere pressure*

[$E_0^\circ$=19,950 cal mole$^{-1}$]

| $T$ | $-\left(\frac{F^\circ-E_0^\circ}{T}\right)$ | $S^\circ$ | $-F^\circ$ | $^a\Delta F^\circ$ | $^a\log_{10}K$ |
|---|---|---|---|---|---|
| | cal deg$^{-1}$ mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ | cal mole$^{-1}$ | $\Delta F^\circ/RT$ 2.3026 |
| °K | | | | | |
| 298.16 | 57.28 | 71.41 | 37,030 | 7,600 | −5.570 |
| 300.00 | 57.37 | 71.57 | 37,160 | 7,830 | −5.703 |
| 400 | 62.00 | 80.31 | 44,750 | 20,650 | −11.283 |
| 500 | 66.57 | 89.37 | 53,230 | 34,070 | −14.894 |
| 600 | 71.12 | 98.28 | 62,620 | 47,840 | −17.426 |
| 700 | 75.64 | 107.14 | 72,900 | 61,830 | −19.305 |
| 800 | 80.11 | 115.55 | 84,040 | 75,950 | −20.748 |
| 900 | 84.50 | 123.58 | 96,000 | 90,120 | −21.884 |
| 1,000 | 88.79 | 131.22 | 108,740 | 104,310 | −22.798 |
| 1,100 | 92.98 | 138.48 | 122,230 | 118,510 | −23.545 |
| 1,200 | 97.06 | 145.39 | 136,420 | 132,690 | −24.166 |
| 1,300 | 101.03 | 151.96 | 151,290 | 146,820 | −24.683 |
| 1,400 | 104.90 | 158.21 | 166,800 | 160,920 | −25.121 |
| 1,500 | 108.65 | 164.17 | 182,930 | 175,000 | −25.498 |

[a] $\Delta F^\circ$ and $K$ are the free-energy change and equilibrium constant, respectively, for the reaction forming cyclohexane from its elements in their standard states at $T$°K.

thermodynamic functions and properties. Table 7 is a comparison of calculated values and the experimental values of $C_p^\circ$ of Montgomery and DeVries [8] and Bennewitz and Rossner [9].

In section XIV the calculated values for the equilibrium constant for the hydrogenation of benzene to cyclohexane are compared with experimental data. The agreement is considered satisfactory.

TABLE 7.—*A comparison of the calculated and experimental values for the heat capacity of cyclohexane above 300° K*

| $T$ | $C_p^\circ$ (calculated) | $C_p^\circ$ (experimental) | Observers [a] |
|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ | |
| 370 | 32.80 | 33.0 | (8) |
| 390 | 34.86 | 35.0 | (8) |
| 410 | 36.88 | 36.8 | (8) |
| 410 | 36.88 | 37.0 | (9) |

[a] (8) J. B. Montgomery and T. DeVries, (9) K. Bennewitz and W. Rossner,

# V. Ethane

The frequency assignment used for ethane was ken from a paper by Stitt [10]. The frequencies centimeters$^{-1}$ were:

*requency due to* C—C *vibration:*

$\omega$=993.

*requencies due to* $CH_3$ *vibrations:*

$\gamma(CH_3)$ rocking motions: 827(2) and 1170(2).

$\delta$(HCH) bending motions: 1375, 1380, 1460(2), and 1465(2).

$\mu$(C—H) stretching motions: 2925(2), 2960(2), and 2980(2).

itt's value of 1,170 cm$^{-1}$ for the "uncertain frequency" of ethane is based upon $D_{3d}$ symmetry d an application of the product rule to the pectra of $C_2H_6$ and $C_2D_6$.

As Kemp and Pitzer [11] have shown and others ve confirmed, there is a mode of hindered rotaon corresponding to rotation of one methyl roup with respect to the other. For low enerjes the motion is vibration, whereas for large nergies it is complete rotation. The height used r the barrier, 2,750 cal mole$^{-1}$, is the value determined by Kistiakowsky, Lacher, and Stitt [12] from low-temperature specific-heat measurement on gaseous ethane.

The ethane molecule has a symmetry number of six. With 1.54 A for the carbon-carbon distance and 1.09 A for the carbon-hydrogen distances, the principal moments of inertia are found to be $10.60\times10^{-40}$ g cm$^2$, $41.84\times10^{-40}$ g cm$^2$, and $41.84\times10^{-40}$ g cm$^2$, whereas the reduced moment for the internal rotation is $2.65\times10^{-40}$ g cm$^2$. The product of the principal moments of inertia is $18.56\times10^{-117}$ g$^3$ cm$^6$.

The values calculated for the various thermodynamic functions of ethane are given in tables 8 and 9.

Table 10 gives a comparison of calculated values of $C_p^\circ$ with experimental values based on the work of Thayer and Stegeman [13], Dailey and Felsing [14] and Eucken and Parts [15].

The calorimetric entropy, $S^\circ$, at 25° C is given by Witt and Kemp [16] as 54.85 cal deg$^{-1}$ mole$^{-1}$. The corresponding statistically calculated $S^\circ$ for 298.16° K is 54.83 cal deg$^{-1}$ mole$^{-1}$.

TABLE 8.—*Heat capacity at constant pressure, heat content, and related quantities of ethane in the ideal gas state*

[$E_0^0 = -16{,}520$ cal mole$^{-1}$]

| $T$ | $\frac{H^\circ - E_0^0}{T}$ | $H^\circ$ | $^a\Delta H^\circ$ | $C_p^\circ$ |
|---|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ | cal mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ |
| 298.16 | 9.59 | −13,660 | −20,240 | 12.59 |
| 300.00 | 9.60 | −13,640 | −20,260 | 12.65 |
| 400 | 10.73 | −12,230 | −21,430 | 15.68 |
| 500 | 12.02 | −10,510 | −22,440 | 18.66 |
| 600 | 13.35 | −8,510 | −23,290 | 21.34 |
| 700 | 14.67 | −6,250 | −23,980 | 23.71 |
| 800 | 15.93 | −3,780 | −24,530 | 25.82 |
| 900 | 17.13 | −1,100 | −24,960 | 27.68 |
| 1,000 | 18.27 | +1,750 | −25,280 | 29.31 |
| 1,100 | 19.34 | 4,750 | −25,500 | 30.75 |
| 1,200 | 20.33 | 7,880 | −25,650 | 32.00 |
| 1,300 | 21.27 | 11,130 | −25,730 | 33.10 |
| 1,400 | 22.15 | 14,480 | −25,760 | 34.05 |
| 1,500 | 22.97 | 17,930 | −25,750 | 34.89 |

[a] $\Delta H^\circ$ is the enthalpy of formation of ethane from its elements in their standard states at the temperature $T$.

TABLE 9.—*Entropy, free energy, and related quantities of ethane in the ideal gas state at 1-atmosphere pressure*

[$E_0^0 = -16{,}520$ cal mole$^{-1}$]

| $T$ | $-\left(\frac{F^\circ - E_0^0}{T}\right)$ | $S^\circ$ | $-F^\circ$ | $^a\Delta F^\circ$ | $^a\log_{10}K$ |
|---|---|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ | cal mole$^{-1}$ | $-\frac{F^\circ/RT}{2.3026}$ |
| 298.16 | 45.25 | 54.83 | 30,010 | −7,850 | 5.756 |
| 300.00 | 45.31 | 54.91 | 30,110 | −7,780 | 5.665 |
| 400 | 48.22 | 58.95 | 35,810 | −3,440 | 1.880 |
| 500 | 50.76 | 62.78 | 41,900 | +1,180 | −0.514 |
| 600 | 53.07 | 66.42 | 48,360 | 5,980 | −2.179 |
| 700 | 55.22 | 69.89 | 55,180 | 10,920 | −3.409 |
| 800 | 57.27 | 73.20 | 62,330 | 15,940 | −4.356 |
| 900 | 59.21 | 76.34 | 69,810 | 21,030 | −5.106 |
| 1,000 | 61.08 | 79.35 | 77,600 | 26,150 | −5.715 |
| 1,100 | 62.87 | 82.21 | 85,680 | 31,310 | −6.220 |
| 1,200 | 64.60 | 84.93 | 94,040 | 36,480 | −6.643 |
| 1,300 | 66.27 | 87.54 | 102,670 | 41,650 | −7.001 |
| 1,400 | 67.88 | 90.03 | 111,560 | 46,820 | −7.309 |
| 1,500 | 69.44 | 92.41 | 120,680 | 52,010 | −7.577 |

[a] $\Delta F^\circ$ and $K$ are the free-energy change and equilibrium constant, respectively, for the reaction forming ethane from its elements in their standard states at $T$°K.

TABLE 10.—*Comparison of the calculated and experimental values for the heat capacity of ethane in the ideal state (above 300° K)*

| $T$ | $C_p^\circ$ (calculated) | $C_p^\circ$ (experimental) | Observers [a] |
|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ | |
| 337.66 | 13.78 | 13.3 | (13) |
| 347.66 | 14.09 | 14.08 | (14) |
| 359.76 | 14.46 | 14.43 | (14) |
| 373.5 | 14.87 | 14.836 | (15) |
| 373.6 | 14.88 | 14.842 | (15) |
| 387.56 | 15.30 | 15.27 | (14) |
| 451.96 | 17.26 | 17.31 | (14) |
| 520.56 | 19.24 | 19.14 | (14) |
| 561.66 | 20.36 | 20.62 | (14) |
| 603.26 | 21.42 | 21.62 | (14) |

[a] (13) V. R. Thayer and G. Stegeman, (14) B. P. Dailey and W. A. [illegible]sing, (15) A. Eucken and A. Parts.

# VI. Ethylene

The fundamental frequencies used for ethylene are those given by Galloway and Barker [17]. The frequencies in centimeters$^{-1}$ are:

*Frequency due to* C=C *vibration*:

1623.3

*Frequencies due to* $CH_2$ *vibrations*:

$\gamma$(C—H) rocking motions: 995, 1055, 949.2, 950, and 825.

$\delta$(HCH) bending motions: 1342.4 and 1412

$\mu$(C—H) stretching motions: 3019.3, 2989, 3105.5, and 3069. The frequency 825 cm$^{-1}$ corresponds to the torsional twist of the C= bond.

The molecule is planar and has a symmet number of 4. The principal moments of iner derived from the ethylene spectra by Galloway a Barker were used. They are $33.84 \times 10^{-40}$ g cm

$^{39}\times10^{-40}$ g cm², and $5.750\times10^{-40}$ g cm². ir product is $5.466\times10^{-117}$ g³ cm⁶. The rmodynamic functions for ethylene are given ables 11 and 12.

In table 13 the calculated values of $C^\circ_p$ are pared with the experimental values from the k of Haas and Stegeman [18], Burcik, Eyster, Yost [19] and Eucken and Parts [15].

The calorimetric entropy, $S^\circ$, at 25° C, is given Egan and Kemp [20] as 52.48 cal deg$^{-1}$ mole$^{-1}$. corresponding statistically calculated $S^\circ$ for 16°K is 52.454 cal deg$^{-1}$ mole$^{-1}$.

BLE 11.—*Heat capacity at constant pressure, heat content d related quantities of ethylene in the ideal gas state*

[$E_0^\circ$=14,530 cal mole$^{-1}$]

| $T$ | $\frac{H^\circ-E_0^\circ}{T}$ | $H^\circ$ | $\Delta H^\circ$ | $C^\circ_p$ |
|---|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ | cal mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ |
| 298.16 | 8.47 | 17,060 | 12,510 | 10.41 |
| 300.00 | 8.49 | 17,080 | 12,490 | 10.46 |
| 400 | 9.28 | 18,240 | 11,780 | 12.91 |
| 500 | 10.24 | 19,650 | 11,150 | 15.18 |
| 600 | 11.23 | 21,270 | 10,610 | 17.12 |
| 700 | 12.19 | 23,070 | 10,170 | 18.78 |
| 800 | 13.11 | 25,020 | 9,800 | 20.23 |
| 900 | 13.97 | 27,110 | 9,490 | 21.49 |
| 1,000 | 14.78 | 29,310 | 9,250 | 22.60 |
| 1,100 | 15.54 | 31,620 | 9,060 | 23.58 |
| 1,200 | 16.25 | 34,020 | 8,920 | 24.43 |
| 1,300 | 16.90 | 36,500 | 8,810 | 25.18 |
| 1,400 | 17.52 | 39,050 | 8,740 | 25.83 |
| 1,500 | 18.09 | 41,670 | 8,690 | 26.41 |

$\Delta H^\circ$ is the enthalpy of formation of ethylene from its elements in their dard states at the temperature $T$.

TABLE 12.—*Entropy, free energy, and related quantities of ethylene in the ideal gas state at 1-atmosphere pressure*

[$E_0^\circ$=14,530 cal mole$^{-1}$]

| $T$ | $-\left(\frac{F^\circ-E_0^\circ}{T}\right)$ | $S^\circ$ | $-F^\circ$ | $\Delta F^\circ$ | $\log_{10}K$ |
|---|---|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ | cal mole$^{-1}$ | $\frac{-\Delta F^\circ/RT}{2.3026}$ |
| 298.16 | 43.98 | 52.45 | −1,420 | 16,290 | −11.943 |
| 300.00 | 44.03 | 52.52 | −1,320 | 16,320 | −11.887 |
| 400 | 46.58 | 55.86 | +4,100 | 17,700 | −9.670 |
| 500 | 48.75 | 58.99 | 9,850 | 19,260 | −8.417 |
| 600 | 50.71 | 61.94 | 15,890 | 20,930 | −7.613 |
| 700 | 52.51 | 64.70 | 22,230 | 22,680 | −7.082 |
| 800 | 54.20 | 67.31 | 28,830 | 24,500 | −6.693 |
| 900 | 55.79 | 69.76 | 35,680 | 26,350 | −6.400 |
| 1,000 | 57.31 | 72.09 | 42,780 | 28,240 | −6.172 |
| 1,100 | 58.75 | 74.29 | 50,100 | 30,150 | −5.990 |
| 1,200 | 60.13 | 76.38 | 57,630 | 32,070 | −5.841 |
| 1,300 | 61.46 | 78.36 | 65,370 | 34,000 | −5.717 |
| 1,400 | 62.73 | 80.25 | 73,300 | 35,940 | −5.611 |
| 1,500 | 63.96 | 82.05 | 81,420 | 37,890 | −5.520 |

$\Delta F^\circ$ and $K$ are the free-energy change and equilibrium constant, respectively, for the reaction forming ethylene from its elements in their standard states at $T$°K.

TABLE 13.—*Comparison of the calculated and experimental values for the heat capacity of ethylene in the ideal gas state above 300° K*

| $T$ | $C^\circ_p$ (calculated) | $C^\circ_p$ (experimental) | Observers * |
|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ | |
| 298.16 | 10.41 | 9.97 | (18) |
| 319.16 | 10.98 | 10.40 | (18) |
| 339.96 | 11.46 | 10.98 | (18) |
| 300.0 | 10.46 | 10.39 | (19) |
| 320.7 | 11.00 | 10.99 | (19) |
| 368.2 | 12.15 | 11.897 | (15) |
| 464.0 | 14.39 | 14.16 | (15) |

* (18) M. E. Haas and G. Stegeman, (19) E. J. Burcik, E. H. Eyster and D. M. Yost, (15) A. Eucken and A. Parts.

# VII. Acetylene

For acetylene, the thermodynamic functions d are those given in a recent paper by Wagman, patrick, Pitzer, and Rossini [21]. Their values e based largely upon an assignment by Wu ] and include the effects of anharmonicity, rotational-vibrational coupling, rotational stretching, and an Euler-Maclaurin series summation correction term. They have been used in preference to our earlier tables, which were based on a table by Gordon [23].

# VIII. Ethyl Alcohol

The thermodynamic functions for ethyl alcohol are given in tables 14 and 15. The frequency assignment used in the calculations of these tables agrees closely with one previously given [24, 25]. The value of 700 $cm^{-1}$, there assigned to the COH angle frequency, was based on earlier papers on methyl alcohol. For the COH angle vibration in methyl alcohol, Borden and Barker [26] later suggested a frequency of 1,030 $cm^{-1}$, and most recently Noether [27] assigned the frequency 1,340 $cm^{-1}$. For the calculations of tables 14 and 15 the observed [28] Raman frequency 1,274 $cm^{-1}$ of ethyl alcohol has been assigned to the COH vibration. To the internal bending vibration of the $CH_2$ group has been assigned the observed Raman frequency 1,455 $cm^{-1}$. Others of the observed Raman frequencies in addition to those listed by Bolla as fundamentals have here been chosen as fundamentals because of their approximate equality with frequencies for similar motions in propane given in the assignment of V. L. Wu and E. F. Barker [29]. Thus the frequencies in centimeters$^{-1}$ that have been used are:

C-C-O *skeleton frequencies:*
883, 1096, and 433.

*Frequencies due to* $CH_2$ *vibrations:*
$\gamma(CH_2)$ rocking motions: 814 and 1051.
$\nu$(C—H) stretching motions: 2930(3).
$\delta$(HCH) bending motions: 1387 and 1455(2).

TABLE 14.—*Heat capacity at constant pressure, heat content, and related quantities of ethyl alcohol in the ideal gas state*

[$E_0^\circ = -52{,}260$ cal $mole^{-1}$]

| $T$ | $\frac{H^\circ - E_0^\circ}{T}$ | $H^\circ$ | $\Delta H^\circ$ | $C_p^\circ$ |
|---|---|---|---|---|
| °K | cal $deg^{-1}$ $mole^{-1}$ | cal $mole^{-1}$ | cal $mole^{-1}$ | cal $deg^{-1}$ $mole^{-1}$ |
| 298.16 | 12.18 | −48,630 | −56,240 | 17.59 |
| 300.00 | 12.22 | −48,600 | −56,260 | 17.66 |
| 400 | 14.00 | −46,660 | −57,250 | 21.00 |
| 500 | 15.70 | −44,410 | −58,110 | 24.09 |
| 600 | 17.33 | −41,860 | −58,780 | 26.81 |
| 700 | 18.86 | −39,060 | −59,320 | 29.18 |
| 800 | 20.28 | −36,030 | −59,710 | 31.25 |
| 900 | 21.61 | −32,810 | −60,000 | 33.07 |
| 1,000 | 22.83 | −29,430 | −60,200 | 34.66 |
| 1,100 | 23.97 | −25,900 | −60,320 | 36.06 |
| 1,200 | 25.02 | −22,240 | −60,370 | 37.28 |
| 1,300 | 25.99 | −18,470 | −60,350 | 38.34 |
| 1,400 | 26.91 | −14,590 | −60,250 | 39.27 |
| 1,500 | 27.75 | −10,630 | −60,190 | 40.08 |

• $\Delta H^\circ$ is the enthalpy of formation of ethyl alcohol from its elements in their standard states at the temperature $T$.

TABLE 15.—*Entropy, free energy, and related quantities of ethyl alcohol in the ideal gas state at 1-atmosphere pressure*

[$E_0^\circ = -52{,}260$ cal $mole^{-1}$]

| $T$ | $-\left(\frac{F^\circ - E_0^\circ}{T}\right)$ | $S^\circ$ | $-F^\circ$ | • $\Delta F^\circ$ | • $\log K$ |
|---|---|---|---|---|---|
| °K | cal $deg^{-1}$ $mole^{-1}$ | cal $deg^{-1}$ $mole^{-1}$ | cal $mole^{-1}$ | cal $mole^{-1}$ | $-\Delta F^\circ/$ |
| 298.16 | 54.27 | 66.45 | 68,440 | −40,010 | 2.329 |
| 300.00 | 54.34 | 66.56 | 68,560 | −39,910 | 20.225 |
| 400 | 58.11 | 72.11 | 75,500 | −34,310 | 18.736 |
| 500 | 61.42 | 77.12 | 82,970 | −28,470 | 12.445 |
| 600 | 64.43 | 81.76 | 90,920 | −22,490 | 8.191 |
| 700 | 67.22 | 86.08 | 99,310 | −16,390 | 5.118 |
| 800 | 69.84 | 90.12 | 108,130 | −10,230 | 2.798 |
| 900 | 72.31 | 93.92 | 117,330 | −4,030 | 0.980 |
| 1,000 | 74.65 | 97.48 | 126,910 | +2,190 | −0.478 |
| 1,100 | 76.88 | 100.85 | 136,830 | 8,430 | −1.673 |
| 1,200 | 79.02 | 104.04 | 147,080 | 14,680 | −2.672 |
| 1,300 | 81.07 | 107.06 | 157,650 | 20,920 | −3.517 |
| 1,400 | 83.03 | 109.94 | 168,500 | 27,170 | −4.239 |
| 1,500 | 84.92 | 112.67 | 179,640 | 33,410 | −4.867 |

• $\Delta F^\circ$ and $K$ are the free-energy change and equilibrium constant, respectively, for the reaction forming ethyl alcohol from its elements in their standard states at $T$°$K$.

*Frequencies due to* $CH_2$ *vibrations:*
$\gamma$ ($CH_2$) waving motions: 814, 1125, and 11
$\nu$ (C—H) stretching motions: 2930(2).
$\delta$ (HCH) bending motion: 1455.

*Frequencies due to* OH *vibrations:*
$\gamma$ (O—H) stretching motion: 3359.
$\delta$ (COH) bending motion: 1274.

The barriers restricting the internal rotations ethyl alcohol have recently been estimated [30] a method involving a correlation of known barr heights in various compounds. According to t calculation, there is a barrier of 1,800 cal mol for the methyl group for the straight fo of the molecule, that is, the form in which the O group is in a plane of symmetry of the molecu and 3,000 cal $mole^{-1}$ for the bent forms, in wh the H of the OH group is on either side of the pla and about 104° from its straight position. T barrier heights for the hydroxyl group are mo complicated. For the methyl group in a positi of minimum energy the calculated potential ener of the hydroxyl group ranges from zero for t straight form to a maximum of 2,375 cal mol when the OH group has rotated about 65°, to minimum of 1,560 cal $mole^{-1}$ at 104°, to anoth maximum of 5,970 cal $mole^{-1}$ at 180°, in whi

osition the OH group extends toward the methyl roup.

The calculations of the thermodynamic functions with these data on the barriers restricting otation have been made by using a natural xtension of Pitzer's [31] steric factor method for arriers with different minimal and maximal alues.

With 1.54 A for the C–C distance, 1.09 A for he C-H distances, 1.42 A for the C-O distance, .96 A for the O—H distance, 105° for the C-O-H ngle and tetrahedral angles for all other angles, he product of the three principal moments of nertia is found to be $2.249 \times 10^{-115}$ g³ cm⁶ for the olecule in the straight form and $2.292 \times 10^{-115}$ g³ m⁶ for the molecule in the bent form. The educed moment of inertia for the $CH_3$ group is $.83 \times 10^{-40}$ g cm² and for the OH group is $1.40 \times 10^{-40}$ cm². In table 16 the calculated values of $C_p^\circ$ re compared with the experimental values by ixon and Greenwood [32], Jatkar [33], Bennewitz nd Rossner [9], and Regnault [34], The calcuted values are higher than the experimental alues except for the value of Regnault at 623° K. his one value may be doubted because of its ntiquity and the experimental difficulties at the levated temperature. It is entirely possible at the present treatment will require revision when more accurate experimental values of the specific heat are available.

TABLE 16.—*Comparison of the calculated and experimental values for the heat capacity of ethyl alcohol in the ideal gas state*

| $T$ | $C_p^\circ$ (calculated) | $C_p^\circ$ (experimental) | Observers[a] |
|---|---|---|---|
| ° K | *cal deg⁻¹ mole⁻¹* | *cal deg⁻¹ mole⁻¹* | |
| 363.16 | 19.76 | 18.49 | (32) |
| 370.26 | 20.00 | 19.86 | (33) |
| 407.16 | 21.24 | 18.75 | (33) |
| 410.16 | 21.34 | 19.6 | (9) |
| 437.16 | 22.20 | 20.8 | (34) |
| 623.16 | 27.38 | 28.2 | (34) |

[a] (32) H. B. Dixon and G. Greenwood, (33) S. K. K. Jatkar, (9) K. Bennewitz and W. Rossner, (34) H. V. Regnault.

The entropy, $S^\circ$, at the boiling point, 351.5° K, based on calorimetric measurements below 298.16° K by Kelley [35] and at higher temperatures by Fiock, Ginnings, and Holton [36] is 69.7 cal deg⁻¹ mole⁻¹. The value interpolated from table 15 is 69.42 cal deg⁻¹ mole⁻¹, agreeing to the uncertainty of the calorimetric value. A similarly obtained calorimetric value of $S^\circ$ at 403.2° K is 72.1 cal deg⁻¹ mole⁻¹, while the corresponding value from table 15 is 72.28 cal deg⁻¹ mole⁻¹.

# IX. Water

The thermodynamic functions of table 17 and 18 r water are based on tables published by Gordon 7]. Gordon took into account the anharmonicities of the $H_2O$ vibrations. For the tables of his paper Gordon's values have been adjusted for otational stretching by using Wilson's theory 8], with a value of the stretching constant determined by Stephenson and McMahon [39]. An djustment for the change in the generally accepted values of the fundamental physical constants has also been made.

The entropy, $S^\circ$, of water at 25° C, was given by Giauque and Archibald [40] as 45.10 cal deg⁻¹ mole⁻¹ on the basis of an investigation of the equilibrium of MgO, $Mg(OH)_2$, and $H_2O$, and the calorimetrically determined entropies of MgO and $Mg(OH)_2$. The value from table 18 is 45.109 cal deg⁻¹ mole⁻¹ at 298.16° K.

TABLE 17.—*Heat capacity at constant pressure, heat content, and related quantities of water in the ideal gas state*

[$E_0^\circ$=−57,106 cal mole$^{-1}$]

| $T$ | $\frac{H^\circ-E_0^\circ}{T}$ | $H^\circ$ | $^a\Delta H^\circ$ | $C_p^\circ$ |
|---|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ | cal mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ |
| 298.16 | 7.934 | −54,740 | −57,799 | 8.028 |
| 300.00 | 7.935 | −54,725 | −57,803 | 8.030 |
| 400 | 7.977 | −53,915 | −58,042 | 8.190 |
| 500 | 8.041 | −53,085 | −58,276 | 8.421 |
| 600 | 8.125 | −52,231 | −58,500 | 8.685 |
| 700 | 8.226 | −51,347 | −58,707 | 8.968 |
| 800 | 8.338 | −50,436 | −58,900 | 9.264 |
| 900 | 8.456 | −49,495 | −59,077 | 9.570 |
| 1,000 | 8.586 | −48,520 | −59,234 | 9.881 |
| 1,100 | 8.715 | −47,520 | −59,379 | 10.185 |
| 1,200 | 8.851 | −46,486 | −59,506 | 10.480 |
| 1,300 | 8.988 | −45,422 | −59,615 | 10.763 |
| 1,400 | 9.125 | −44,333 | −59,715 | 11.031 |
| 1,500 | 9.260 | −43,217 | −59,801 | 11.279 |

$^a\Delta H^\circ$ is the enthalpy of formation of water from its elements in their standard states at the temperature $T$.

TABLE 18.—*Entropy, free energy and related quantities of water in the ideal gas state at 1-atmosphere pressure*

[$E_0^\circ$=−57,106 cal mole$^{-1}$]

| $T$ | $-\left(\frac{F^\circ-E_0^\circ}{T}\right)$ | $S^\circ$ | $-F^\circ$ | $^a\Delta F^\circ$ | $^a\log K$ |
|---|---|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ | cal mole$^{-1}$ | $\frac{-\Delta F^\circ/RT}{2.3026}$ |
| 298.16 | 37.175 | 45.109 | 68,190 | −54,638 | 40.030 |
| 300.00 | 37.224 | 45.159 | 68,273 | −54,618 | 39.796 |
| 400 | 39.512 | 47.489 | 72,911 | −53,521 | 29.263 |
| 500 | 41.299 | 49.340 | 77,756 | −52,363 | 22.866 |
| 600 | 42.773 | 50.898 | 82,770 | −51,160 | 18.635 |
| 700 | 44.032 | 52.258 | 87,928 | −49,918 | 15.585 |
| 800 | 45.137 | 53.475 | 93,216 | −48,648 | 13.290 |
| 900 | 46.127 | 54.583 | 98,620 | −47,357 | 11.500 |
| 1,000 | 47.023 | 55.609 | 104,129 | −46,046 | 10.062 |
| 1,100 | 47.849 | 56.564 | 109,740 | −44,722 | 8.882 |
| 1,200 | 48.612 | 57.463 | 115,440 | −43,381 | 7.901 |
| 1,300 | 49.326 | 58.314 | 121,230 | −42,036 | 7.067 |
| 1,400 | 49.997 | 59.122 | 127,102 | −40,681 | 6.351 |
| 1,500 | 50.631 | 59.891 | 133,052 | −39,314 | 5.728 |

$^a\Delta F^\circ$ and K are the free-energy change and equilibrium constant, respectively, for the reaction forming water from its elements in their standard states at $T$°K.

# X. Graphite

The thermodynamic functions for graphite are given in tables 19 and 20. They were obtained by tabular integration of the specific heat of graphite which has been measured [41, 42, 43, 44, 45] within the range −244 to 1,200°C. The values used for specific heats at the higher temperatures were also based in part on specific-heat measurements [46] on a carbon filament from 1,200° to 2,100° C.

TABLE 19.—*Heat capacity at constant pressure, heat content, $H^\circ$, and $(H^\circ-E_0^\circ)/T$ for graphite*

[$E_0^\circ$=0]

| $T$ | $\frac{H^\circ-E_0^\circ}{T}$ | $H^\circ$ | $C_p^\circ$ |
|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ |
| 298.16 | 0.842 | 251 | 2.055 |
| 300.00 | .850 | 255 | 2.071 |
| 400 | 1.256 | 503 | 2.852 |
| 500 | 1.642 | 821 | 3.488 |
| 600 | 1.993 | 1,196 | 3.991 |
| 700 | 2.309 | 1,616 | 4.391 |
| 800 | 2.590 | 2,072 | 4.720 |
| 900 | 2.841 | 2,557 | 4.972 |
| 1,000 | 3.064 | 3,064 | 5.150 |
| 1,100 | 3.262 | 3,588 | 5.300 |
| 1,200 | 3.437 | 4,124 | 5.422 |
| 1,300 | 3.593 | 4,671 | 5.520 |
| 1,400 | 3.734 | 5,227 | 5.600 |
| 1,500 | 3.862 | 5,793 | 5.669 |

TABLE 20.—*Entropy, free energy, and the free-energy function for graphite*

[$E_0^\circ$=0]

| $T$ | $-\left(\frac{F^\circ-E_0^\circ}{T}\right)$ | $S^\circ$ | $-F^\circ$ |
|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ |
| 298.16 | 0.525 | 1.367 | 157 |
| 300.00 | 0.529 | 1.379 | 159 |
| 400 | .830 | 2.088 | 332 |
| 500 | 1.153 | 2.795 | 577 |
| 600 | 1.484 | 3.477 | 890 |
| 700 | 1.815 | 4.124 | 1,271 |
| 800 | 2.142 | 4.732 | 1,714 |
| 900 | 2.462 | 5.303 | 2,216 |
| 1,000 | 2.774 | 5.838 | 2,774 |
| 1,100 | 3.075 | 6.337 | 3,382 |
| 1,200 | 3.367 | 6.804 | 4,040 |
| 1,300 | 3.648 | 7.241 | 4,742 |
| 1,400 | 3.919 | 7.653 | 5,487 |
| 1,500 | 4.181 | 8.043 | 6,272 |

# XI. Hydrogen

The thermodynamic functions for hydrogen given in tables 21 and 22 are from an unpublished compilation of thermal properties of hydrogen [47].

TABLE 21.—*Heat capacity at constant pressure, heat content, and related quantities of hydrogen in the ideal gas state*

[$E_0^\circ$=0]

| $T$ | $\frac{H^\circ-E_0^\circ}{T}$ | $H^\circ$ | $C_p^\circ$ |
|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ |
| 298.16 | 6.787 | 2023.8 | 6.891 |
| 300.00 | 6.788 | 2036.4 | 6.894 |
| 400 | 6.827 | 2731.0 | 6.975 |
| 500 | 6.859 | 3429.5 | 6.993 |
| 600 | 6.883 | 4129.5 | 7.009 |
| 700 | 6.902 | 4831.7 | 7.036 |
| 800 | 6.922 | 5537.3 | 7.081 |
| 900 | 6.943 | 6248.3 | 7.142 |
| 1,000 | 6.966 | 6966.2 | 7.219 |
| 1,100 | 6.993 | 7,692 | 7.307 |
| 1,200 | 7.023 | 8,428 | 7.406 |
| 1,300 | 7.057 | 9,174 | 7.511 |
| 1,400 | 7.093 | 9,930 | 7.617 |
| 1,500 | 7.131 | 10,697 | 7.720 |

TABLE 22.—*Entropy*[a]*, free energy*[a]*, and related quantities of hydrogen in the ideal gas state at 1-atmosphere pressure*

[$E_0^\circ$=0]

| $T$ | $-\left(\frac{F^\circ-E_0^\circ}{T}\right)$ | $S^\circ$ | $-F^\circ$ |
|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ |
| 298.16 | 24.420 | 31.207 | 7,281 |
| 300.00 | 24.462 | 31.250 | 7,339 |
| 400 | 26.420 | 33.247 | 10,568 |
| 500 | 27.947 | 34.806 | 13,974 |
| 600 | 29.200 | 36.083 | 17,520 |
| 700 | 30.263 | 37.165 | 21,184 |
| 800 | 31.187 | 38.109 | 24,950 |
| 900 | 32.003 | 38.946 | 28,803 |
| 1,000 | 32.735 | 39.701 | 32,735 |
| 1,100 | 33.400 | 40.393 | 36,740 |
| 1,200 | 34.010 | 41.033 | 40,812 |
| 1,300 | 34.572 | 41.629 | 44,944 |
| 1,400 | 35.096 | 42.189 | 49,134 |
| 1,500 | 35.588 | 42.719 | 53,382 |

[a] The nuclear spin entropy has been subtracted so that these values may be used directly in connection with chemical reactions.

# XII. Oxygen

Thermodynamic functions for oxygen are given in tables 23 and 24. These are based on the tables of Johnston and Walker [48] but have been adjusted to be consistent with a more recent value of Curry and Herzberg [49] for the vibrational frequency and with present generally accepted values of the fundamental physical constants. Curry and Herzberg represented the term values in cm$^{-1}$ of the vibrational levels, with quantum number $v$, relative to the lowest vibrational level ($v$=0) by the formula

$$(1568.33v-11.993v^2+0.0517v^3-0.00143v^4).$$

The earlier, or 1933, tables of Johnston and Walker, from which the tables of this paper were obtained by adjustment, were based on the formula

$$(1565.37v-11.37v^2).$$

TABLE 23.—*Heat capacity at constant pressure, heat content and related quantities of oxygen in the ideal gas state*

[$E_0^\circ$=0]

| $T$ | $\frac{H^\circ-E_0^\circ}{T}$ | $H^\circ$ | $C_p^\circ$ |
|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ |
| 298.16 | 6.941 | 2,069.8 | 7.019 |
| 300.00 | 6.942 | 2,082.7 | 7.021 |
| 400 | 6.981 | 2,792.6 | 7.194 |
| 500 | 7.047 | 3,523.5 | 7.430 |
| 600 | 7.131 | 4,278.6 | 7.669 |
| 700 | 7.223 | 5,056.4 | 7.882 |
| 800 | 7.317 | 5,853.8 | 8.062 |
| 900 | 7.409 | 6,667.7 | 8.211 |
| 1,000 | 7.495 | 7,495.3 | 8.335 |
| 1,100 | 7.576 | 8,334 | 8.439 |
| 1,200 | 7.652 | 9,183 | 8.528 |
| 1,300 | 7.723 | 10,040 | 8.606 |
| 1,400 | 7.789 | 10,904 | 8.675 |
| 1,500 | 7.849 | 11,774 | 8.739 |

TABLE 24.—*Entropy, free energy, and related quantities of oxygen in the ideal gas state at 1-atmosphere pressure*

[$E_0^\circ$=0]

| $T$ | $-\left(\frac{F^\circ-E_0^\circ}{T}\right)$ | $S^\circ$ | $-F^\circ$ |
|---|---|---|---|
| °K | cal deg$^{-1}$ mole$^{-1}$ | cal deg$^{-1}$ mole$^{-1}$ | cal mole$^{-1}$ |
| 298.16 | 42.067 | 49.008 | 12,543 |
| 300.00 | 42.110 | 49.052 | 12,633 |
| 400 | 44.112 | 51.093 | 17,645 |
| 500 | 45.676 | 52.723 | 22,838 |
| 600 | 46.968 | 54.099 | 28,181 |
| 700 | 48.074 | 55.297 | 33,652 |
| 800 | 49.045 | 56.362 | 39,236 |
| 900 | 49.911 | 57.320 | 44,920 |
| 1,000 | 50.697 | 58.192 | 50,697 |
| 1,100 | 51.415 | 58.991 | 56,556 |
| 1,200 | 52.078 | 59.730 | 62,494 |
| 1,300 | 52.692 | 60.415 | 68,501 |
| 1,400 | 53.267 | 61.056 | 74,574 |
| 1,500 | 53.808 | 61.657 | 80,712 |

# XIII. Heats of Formation at 0°K

The heats of formation at 0°K, $E_0^\circ$, given in the tables of this paper were obtained from values of heats of formation at ordinary temperatures.

The calculation of $E_0^\circ$ for 1,3-butadiene is discussed in reference [4].

The heats of formation of the other substances at 298.16°K were based on values published or privately communicated by Rossini and his coworkers [50, 51, 52, 53].

Values of $E_0^\circ$ adopted for this paper should not be expected to agree exactly with previously published values of $E_0^\circ$, even though they are based on the same heats of formation at 298.16°K, as the values of $E_0^\circ$ involve also values of $H^\circ - E_0^\circ$, and the effects of rounding off values are also present.

# XIV. Equilibrium Constants

The equilibrium constants of the reactions listed in section I are given in tables 25 to 29 as functions of the temperature from 298.16° to 1,500°K. These equilibrium constants were derived from data in tables 1 to 26 of this paper and tables for the *n*-butenes in reference [4].

The equilibrium constants $K_p$ are for pressures expressed in atmosperes, as the pressure chosen for the specification of the standard state is 1 atmosphere.

$$\text{Log}_{10} K_p = -\Delta F^\circ/(2.3026RT),$$

where $\Delta F^\circ$ is the difference between the sums of the free energies of the products and of the reactants of the reaction to which $K_p$ applies, the free energies being those of pure substances in the ideal gaseous state at 1 atmosphere pressure and at temperature $T$°K. The values of $K_p$ in tables 25 to 29 are therefore calculated for reactions in the ideal gaseous state and differ from equilibrium constants for actual real gas conditions by amounts determined by the departure of real gas mixtures from ideal gas behavior.

Some reactions for which the equilibrium constants are given in tables 25 to 29 are discussed in the following paragraphs.

$$C_6H_6 + 3H_2 \rightleftharpoons C_6H_{12} \text{ (cyclohexane)}$$

The equilibrium constants for the hydrogenation of benzene to cyclohexane have been determined experimentally by Burrows and Lucarini [54] and by Zharkova and Frost [55]. Their experimentally determined constants are compared in table 30 with the calculated constants derived from the free energy data of this paper.

The equilibrium constant (table 25) varies rapidly with temperature. At ordinary temperatures, mixtures of benzene and hydrogen are very much less stable thermodynamically than cyclohexane, whereas at high temperatures of the order of 1,000° K, cyclohexane is very much less stable. Because of the rapid variation of $K_p$ with temperature, experimental determinations of the equilibrium constant have been limited practically to a fifty degree range of temperatures from about 500° to 550° K. Considering this rapid variation, the agreement of the experimental and calculated equilibrium constants in table 30 is considered satisfactory.

TABLE 25.—*Equilibrium constants $K_p$ (pressures in atmospheres) for the reactions:*

(1) $C_6H_6(g) + 3H_2 \rightleftharpoons C_6H_{12}$(cyclohexane, g).
(2) $C_6H_{12}$(cyclohexane, g) $\rightleftharpoons C_4H_6$(1,3-butadiene) $+ C_2H_4 + H_2$
(3) $C_6H_{12}$(cyclohexane, g) $\rightleftharpoons C_4H_6$(1,3-butadiene) $+ C_2H_4$.

| $T$ | $K_{p(1)}$ | $K_{p(2)}$ | $K_{p(3)}$ |
|---|---|---|---|
| °K | atm$^{-3}$ | atm$^{2}$ | atm |
| 298.16 | $1.43\times10^{17}$ | $8.32\times10^{-44}$ | $4.15\times10^{-9}$ |
| 300.00 | $8.53\times10^{16}$ | $1.69\times10^{-42}$ | $6.04\times10^{-8}$ |
| 400 | $7.06\times10^{7}$ | $6.61\times10^{-21}$ | $2.36\times10^{-4}$ |
| 500 | $1.85\times10^{3}$ | $2.94\times10^{-12}$ | $2.35\times10^{-4}$ |
| 600 | $3.05\times10^{-1}$ | $4.12\times10^{-6}$ | $1.12\times10^{-2}$ |
| 700 | $5.66\times10^{-4}$ | $1.95\times10^{-4}$ | 0.916 |
| 800 | $4.94\times10^{-7}$ | 0.113 | 24.5 |
| 900 | $1.23\times10^{-9}$ | 15.7 | $3.10\times10^{3}$ |
| 1,000 | $6.49\times10^{-12}$ | $8.03\times10^{3}$ | $2.30\times10^{5}$ |
| 1,100 | $5.89\times10^{-14}$ | $1.97\times10^{5}$ | $1.16\times10^{6}$ |
| 1,200 | $8.09\times10^{-16}$ | $2.79\times10^{6}$ | $4.40\times10^{6}$ |
| 1,300 | $1.53\times10^{-17}$ | $2.56\times10^{6}$ | $1.33\times10^{7}$ |
| 1,400 | $3.75\times10^{-19}$ | $1.69\times10^{7}$ | $3.40\times10^{7}$ |
| 1,500 | $1.11\times10^{-20}$ | $8.61\times10^{7}$ | $7.55\times10^{7}$ |

$$C_6H_{12} \text{ (cyclohexane)} \rightleftharpoons C_4H_6 \text{ (1,3-butadiene)} + C_2H_4 + H_2$$

In the thermal cracking of cyclohexane for commercial production of butadiene, cyclohexane is passed through a tube into which superheated steam at a high temperature (about 1,300° K) is injected to raise the temperature of the cyclo-

BLE 26.—*Equilibrium constants $K_p$ (pressures in atmospheres) for the reactions:*

$C_6H_{12}$(cyclohexane, g)$\rightleftharpoons C_6H_6$(1,3-butadiene)$+C_2H_2+2H_2$.

$C_6H_{12}$(cyclohexane, g)$\rightleftharpoons\frac{3}{2}C_6H_6$(1,3-butadiene)$+\frac{3}{2}H_2$

$C_6H_{12}$(cyclohexane, g)$\rightleftharpoons 3C_2H_4$.

$2C_2H_4\rightleftharpoons C_4H_6$(1,3-butadiene)$+H_2$.

| $T$ | $K_{p(1)}$ | $K_{p(2)}$ | $K_{p(3)}$ | $K_{p(4)}$ |
|---|---|---|---|---|
| °K | $atm^2$ | $atm^2$ | $atm^2$ | $atm^2$ |
| 298.16 | $1.61\times10^{-48}$ | $3.24\times10^{-45}$ | $5.50\times10^{-31}$ | $1.51\times10^{-4}$ |
| 300.00 | $5.20\times10^{-48}$ | $6.64\times10^{-44}$ | $1.10\times10^{-30}$ | $1.84\times10^{-4}$ |
| 400 | $8.83\times10^{-38}$ | $3.93\times10^{-33}$ | $1.88\times10^{-18}$ | $3.52\times10^{-3}$ |
| 500 | $1.78\times10^{-30}$ | $2.40\times10^{-26}$ | $4.40\times10^{-11}$ | $6.08\times10^{-2}$ |
| 600 | $2.95\times10^{-25}$ | $4.26\times10^{-4}$ | $3.86\times10^{-6}$ | $1.07\times10^{-1}$ |
| 700 | $2.99\times10^{-21}$ | $2.54\times10^{-4}$ | $1.14\times10^{-3}$ | $1.70\times10^{-1}$ |
| 800 | $8.83\times10^{-7}$ | $1.75\times10^{-3}$ | 4.67 | $2.42\times10^{-1}$ |
| 900 | $2.66\times10^{-3}$ | 2.84 | $4.83\times10^{2}$ | $3.26\times10^{-1}$ |
| 1,000 | 1.59 | $1.64\times10^{2}$ | $1.91\times10^{4}$ | $4.20\times10^{-1}$ |
| 1,100 | $2.94\times10^{2}$ | $4.52\times10^{2}$ | $3.76\times10^{5}$ | $5.25\times10^{-1}$ |
| 1,200 | $2.23\times10^{4}$ | $7.01\times10^{4}$ | $4.40\times10^{6}$ | $6.34\times10^{-1}$ |
| 1,300 | $8.53\times10^{5}$ | $7.05\times10^{6}$ | $3.40\times10^{7}$ | $7.53\times10^{-1}$ |
| 1,400 | $1.90\times10^{7}$ | $5.01\times10^{8}$ | $1.94\times10^{8}$ | $8.73\times10^{-1}$ |
| 1,500 | $2.76\times10^{8}$ | $2.72\times10^{7}$ | $8.67\times10^{8}$ | $9.93\times10^{-1}$ |

BLE 27.—*Equilibrium constant $K_p$ ($atm^{-1}$), for the reaction $2C_2H_4\rightleftharpoons n-C_4H_8$ (1-butene, cis and trans-2-utene and the equilibrium mixture of the n-butenes)*

| $T$ | $K_p$($atm^{-1}$) 1-butene | $K_p$($atm^{-1}$) cis-2-butene | $K_p$($atm^{-1}$) trans-2-butene | $K_p$($atm^{-1}$) equilibrium mixture n-butenes |
|---|---|---|---|---|
| °K | | | | |
| 298.16 | $1.38\times10^{21}$ | $1.27\times10^{12}$ | $4.67\times10^{12}$ | $6.08\times10^{12}$ |
| 300.00 | $1.07\times10^{21}$ | $9.70\times10^{11}$ | $3.52\times10^{12}$ | $4.59\times10^{12}$ |
| 400 | $3.40\times10^{8}$ | $1.48\times10^{7}$ | $3.60\times10^{7}$ | $5.42\times10^{7}$ |
| 500 | $6.84\times10^{3}$ | $1.85\times10^{4}$ | $3.63\times10^{4}$ | $6.16\times10^{4}$ |
| 600 | $1.06\times10^{3}$ | $2.01\times10^{3}$ | $3.51\times10^{3}$ | $6.58\times10^{3}$ |
| 700 | 5.86 | 8.57 | 1.39×10 | 2.83×10 |
| 800 | $6.55\times10^{-1}$ | $7.80\times10^{-1}$ | 1.21 | 2.64 |
| 900 | $1.20\times10^{-1}$ | $1.21\times10^{-1}$ | $1.81\times10^{-1}$ | $4.22\times10^{-1}$ |
| 1,000 | $3.11\times10^{-2}$ | $2.74\times10^{-2}$ | $4.00\times10^{-2}$ | $9.85\times10^{-2}$ |
| 1,100 | $1.04\times10^{-2}$ | $8.20\times10^{-3}$ | $1.18\times10^{-2}$ | $3.04\times10^{-2}$ |
| 1,200 | $4.17\times10^{-3}$ | $3.01\times10^{-3}$ | $4.26\times10^{-3}$ | $1.14\times10^{-2}$ |
| 1,300 | $1.95\times10^{-3}$ | $1.30\times10^{-3}$ | $1.82\times10^{-3}$ | $5.07\times10^{-3}$ |
| 1,400 | $1.02\times10^{-3}$ | $6.32\times10^{-4}$ | $8.85\times10^{-4}$ | $2.54\times10^{-3}$ |
| 1,500 | $5.82\times10^{-4}$ | $3.40\times10^{-4}$ | $4.69\times10^{-4}$ | $1.30\times10^{-3}$ |

TABLE 28.—*Equilibrium constants $K_p$ (pressures in atmospheres) for the reactions:*

(1) $C_2H_6\rightleftharpoons C_2H_4+H_2$.
(2) $2C_2H_5OH\rightleftharpoons C_4H_6$(1,3-butadiene)$+2H_2O+H_2$.
(3) $C_2H_4+H_2O\rightleftharpoons C_2H_5OH$.
(4) $C_2H_4+C_2H_2\rightleftharpoons C_4H_6$(1,3-butadiene).

| $T$ | $K_{p(1)}$ | $K_{p(2)}$ | $K_{p(3)}$ | $K_{p(4)}$ |
|---|---|---|---|---|
| °K | atm | $atm^2$ | $atm^{-1}$ | $atm^{-1}$ |
| 298.16 | $2.00\times10^{-18}$ | $5.43\times10^{-6}$ | 1.66×10 | $7.78\times10^{21}$ |
| 300.00 | $2.80\times10^{-18}$ | $6.97\times10^{-6}$ | 1.49×10 | $5.13\times10^{21}$ |
| 400 | $2.82\times10^{-13}$ | $1.57\times10^{-1}$ | $1.49\times10^{-1}$ | $2.64\times10^{14}$ |
| 500 | $1.25\times10^{-8}$ | 7.46×10 | $9.47\times10^{-3}$ | $1.10\times10^{12}$ |
| 600 | $3.68\times10^{-6}$ | $4.90\times10^{3}$ | $1.51\times10^{-3}$ | $1.30\times10^{7}$ |
| 700 | $2.12\times10^{-4}$ | $1.00\times10^{5}$ | $4.13\times10^{4}$ | $1.10\times10^{3}$ |
| 800 | $4.60\times10^{-3}$ | $9.66\times10^{5}$ | $1.58\times10^{-4}$ | $3.08\times10^{3}$ |
| 900 | $5.08\times10^{-2}$ | $5.66\times10^{6}$ | $7.59\times10^{-6}$ | $1.93\times10^{3}$ |
| 1,000 | 0.349 | $2.31\times10^{7}$ | $4.27\times10^{-6}$ | 21.2 |
| 1,100 | 1.70 | $7.28\times10^{7}$ | $2.68\times10^{-6}$ | 3.53 |
| 1,200 | 6.34 | $1.85\times10^{8}$ | $1.85\times10^{-6}$ | 0.792 |
| 1,300 | 19.2 | $4.08\times10^{8}$ | $1.36\times10^{-6}$ | 0.226 |
| 1,400 | 49.9 | $7.92\times10^{8}$ | $1.04\times10^{-6}$ | $7.78\times10^{-2}$ |
| 1,500 | 114.0 | $1.40\times10^{9}$ | $0.84\times10^{-6}$ | $3.10\times10^{-2}$ |

TABLE 29.—*Equilibrium constants $K_p$ (pressures in atmospheres) for the reactions:*

(1) $C_2H_4\rightleftharpoons C_2H_2+H_2$.
(2) $C_2H_6\rightleftharpoons C_2H_2+2H_2$.
(3) $C_2H_4+C_4H_6$(1,3-butadiene)$\rightleftharpoons C_6H_6(g)+2H_2$.
(4) $2C_4H_6$(1,3-butadiene)$\rightleftharpoons C_6H_6(g)+C_2H_4+H_2$.

| $T$ | $K_{p(1)}$ | $K_{p(2)}$ | $K_{p(3)}$ | $K_{p(4)}$ |
|---|---|---|---|---|
| °K | atm | $atm^2$ | atm | atm |
| 298.16 | $1.94\times10^{-35}$ | $3.88\times10^{-49}$ | $8.41\times10^{14}$ | $5.57\times10^{13}$ |
| 300.00 | $3.00\times10^{-35}$ | $8.41\times10^{-49}$ | $6.92\times10^{14}$ | $4.49\times10^{13}$ |
| 400 | $1.34\times10^{-17}$ | $3.77\times10^{-29}$ | $2.14\times10^{12}$ | $6.08\times10^{11}$ |
| 500 | $6.08\times10^{-13}$ | $7.60\times10^{-21}$ | $1.84\times10^{10}$ | $2.75\times10^{10}$ |
| 600 | $8.22\times10^{-10}$ | $3.03\times10^{-15}$ | $7.96\times10^{8}$ | $7.46\times10^{9}$ |
| 700 | $1.54\times10^{-7}$ | $3.27\times10^{-11}$ | $9.08\times10^{7}$ | $5.35\times10^{9}$ |
| 800 | $7.84\times10^{-6}$ | $3.61\times10^{-8}$ | $1.79\times10^{7}$ | $7.43\times10^{8}$ |
| 900 | $1.69\times10^{-4}$ | $8.59\times10^{-6}$ | $5.15\times10^{6}$ | $1.58\times10^{8}$ |
| 1,000 | $1.98\times10^{-3}$ | $6.92\times10^{-4}$ | $1.92\times10^{6}$ | $4.57\times10^{7}$ |
| 1,100 | $1.49\times10^{-2}$ | $2.53\times10^{-2}$ | $8.61\times10^{5}$ | $1.64\times10^{7}$ |
| 1,200 | $8.00\times10^{-2}$ | 0.507 | $4.44\times10^{5}$ | $7.00\times10^{6}$ |
| 1,300 | 0.333 | 6.40 | $2.54\times10^{5}$ | $3.37\times10^{6}$ |
| 1,400 | 1.12 | 56.0 | $1.57\times10^{5}$ | $1.80\times10^{6}$ |
| 1,500 | 3.21 | 260.0 | $1.04\times10^{5}$ | $1.05\times10^{6}$ |

TABLE 30.—*A comparison of calculated and experimental values for the equilibrium constant $K_p$ for the reaction:*

$$C_6H_6+3H_2 \rightleftharpoons C_6H_{12}$$

| $T$ | $K_p$ (calculated) | $K_p$ (experimental) | Observers [a] |
|---|---|---|---|
| °K | $atm^{-2}$ | $atm^{-2}$ | |
| 503.1 | 134.0 | 135.0 | (55) |
| 503.3 | 132.0 | 104.0 | (55) |
| 503.5 | 129.0 | 77.0 | (55) |
| 522.6 | 19.5 | 11.0 | (55) |
| 522.6 | 19.5 | 10.7 | (55) |
| 523.1 | 18.6 | 12.6 | (55) |
| 523.4 | 18.1 | 11.7 | (55) |
| 523.4 | 18.1 | 16.0 | (55) |
| 523.6 | 17.8 | 15.4 | (55) |
| 540.0 | 3.92 | 5.10 | (54) |
| 540.0 | 3.92 | 5.49 | (54) |
| 540.0 | 3.92 | 5.40 | (54) |
| 540.0 | 3.92 | 5.51 | (54) |
| 548.1 | 1.91 | 1.61 | (55) |
| 548.1 | 1.91 | 1.56 | (55) |
| 548.6 | 1.84 | 1.18 | (55) |
| 549.6 | 1.68 | 1.11 | (55) |
| 553.2 | 1.23 | 1.52 | (54) |
| 553.2 | 1.23 | 1.60 | (54) |
| 553.2 | 1.23 | 1.63 | (54) |

[a] (54) G. H. Burrows and C. Lucarini, (55) Z. R. Zharkova and A. V. Frost.

hexane from about 900° to 1,000° K. Under these conditions it is probable that the above reaction is one of the principal primary reactions taking place.

As will be seen from table 26 the square of the concentration of $C_2H_4$ in thermodynamic equilibrium with butadiene at 1,000° K is about 24 times the product of the concentrations of $C_4H_6$ and $H_2$. For the same concentration of $H_2$ and $C_4H_6$ this means that the concentration of $C_2H_4$ is about 5 times that of butadiene. Schneider and Frolich [56] have shown that butadiene and hydrogen are the principal initial products resulting from the pyrolysis of etheylene, from which it would be inferred that the rate of cracking of butadiene to form ethylene must be appreciable. Hence in the production of butadiene from cyclohexane, the temperature of a cracked cyclohexane product high in butadiene should be lowered in a reasonably short time. As in the cracking reaction of cyclohexane, butadiene, and ethylene are formed in equal concentrations the establishment of thermodynamic equilibrium between $C_2H_4$, $C_4H_6$, and $H_2$ decreases the yield of butadiene.

$C_6H_{12}$ (cyclohexane)$\rightleftharpoons C_4H_6$ (1, 3-butadiene)+C

Ethane is not formed to any appreciable ex as a primary product in the thermal cracking cyclohexane. The equilibrium indicated by equation heading this subsection is probably result of the two reactions:

$$C_6H_{12} \rightleftharpoons C_4H_6+C_2H_4+H_2$$

$$C_2H_4+H_2 \rightleftharpoons C_2H_6$$

With increase of pressure on the gaseous syst the concentration of ethane will increase relati to the concentration of ethylene in accorda with the law of mass action.

$$2C_2H_4 \rightleftharpoons C_4H_6+H_2$$

In the pyrolysis of ethylene at 725° C (1,0 K) Schneider and Frolich [56] found that 72 p cent of the product initially formed is $C_4H_6$ $H_2$. According to these authors the rate of reaction is first order or less, indicating an in mediate reaction, possibly that of formation of excited ethylene molecule or a free vinyl radi

$$2C_2H_4 \rightleftharpoons n\text{-}C_4H_8$$

Schneider and Frolich [61] observed that bute are initial products in the pyrolysis of $C_2H_4$. table 27 are given the equilibrium constants the separate reactions forming 1-butene, ci butene, *trans*-2-butene and an equilibrium m ture of *n*-butenes. The thermodynamic data the butenes used in the calculation of these eq librium constants were taken from reference

$$C_2H_6 \rightleftharpoons C_2H_4+H_2$$

Experimental determinations of the equilibri constant $K_p$ for this reaction have been made Kistiakowsky [57], Frey and Huppke [58], Vid ski and Vinikova [59], Travers and Pearce [ Pease and Durgan [61], and Travers and Hoc [62]. In table 31 their results are compared w calculated values interpolated from table 2

$$2C_2H_5OH\ (g) \rightleftharpoons C_4H_6\ (1,3\text{-butadiene})+2H_2O\ (g)+H_2$$

In the Lebedev process for making butadie ethyl alcohol is passed over a mixed dehydroge tion-dehydration catalyst at a temperature about 700° K. The over-all reaction of process is as written above. It is likely, howe that intermediate reactions are involved.

TABLE 31.—*A comparison of calculated and experimental values for the equilibrium constant $K_p$ for the reaction:*

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$

| $K$ | $K_p$ (calculated) | $K_p$ (experimental) | Observers* |
|---|---|---|---|
| °$K$ | *atm* | *atm* | |
| 653 | $3.68\times10^{-3}$ | $4.04\times10^{-3}$ | (57) |
| 673 | $7.98\times10^{-3}$ | $8.2\times10^{-3}$ | (58) |
| 723 | $4.63\times10^{-2}$ | $5.16\times10^{-2}$<br>$5.6\times10^{-2}$ | (57)<br>(58) |
| 773 | $2.16\times10^{-1}$ | $3.2\times10^{-1}$<br>$2.4\times10^{-1}$ | (59)<br>(58) |
| 823 | $8.41\times10^{-1}$ | $7.4\times10^{-1}$ | (60) |
| 843 | 0.0139 | 0.0153 | (60) |
| 863 | .0223 | .0244<br>.0245 | (60)<br>(61) |
| 873 | .0281 | .031 | (61) |
| 883 | .0351 | .0359<br>.033 | (60)<br>(62) |
| 893 | .0438 | .0446 | (60) |
| 903 | .0542 | .054 | (60) |
| 923 | .0822 | .082<br>.078 | (61)<br>(60) |
| 973 | .216 | .20 | (61) |

*(57) G. B. Kistiakowsky, (58) F. E. Frey and W. F. Huppke, recalculated, G. B. Kistiakowsky, H. Romeyn, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, (59) A. A. Videnski and S. G. Vinikova, (60) M. W. Travers and T. J. P. Pearce, (61) R. N. Pease and E. S. Durgan, (62) M. W. Travers and L. E. Hockin.

$$C_2H_4 + H_2O \rightleftharpoons C_2H_5OH$$

Experimental determinations of $K_p$ for this reaction have been made by Stanley, Youell and Dymock [63], Appleby, Glass, and Horsley [64], and Bliss and Dodge [65]. The experimental values of $K_p$ are compared with calculated values in table 32.

$$C_2H_4 + C_4H_6 \text{ (1, 3-butadiene)} \rightleftharpoons C_6H_6 \text{ (g)} + 2H_2$$

Schneider and Frolich [56] found that benzene was the most abundant single initial product resulting from the pyrolysis of a mixture of ethylene (90 percent) and butadiene (10 percent) at 1,000° K and one-fifth of an atmosphere. It is probable that there is an intermediate metastable complex formed by $C_2H_4$ and $C_4H_6$, possibly the triolefin $C_6H_8$, which breaks down, giving $C_6H_6$.

$$2C_4H_6 \text{ (1,3-butadiene)} \rightleftharpoons C_6H_8 \text{ (g)} + C_2H_4 + H_2$$

Schneider and Frolich [56] suggest that benzene may be formed as a result of a coalescence of two butadiene molecules.

TABLE 32.—*A comparison of calculated and experimental values for the equilibrium constant $K_p$ of the reaction:*

$$C_2H_4 + H_2O \rightleftharpoons C_2H_5OH$$

| $T$ | $K_p$ (calculated) | $K_p$ (experimental) | Observers* |
|---|---|---|---|
| °$K$ | $atm^{-1}$ | $atm^{-1}$ | |
| 418 | $8.28\times10^{-2}$ | $6.8\times10^{-2}$ | (68) |
| 448 | $3.42\times10^{-2}$ | $3.6\times10^{-2}$<br>$2.93\times10^{-2}$ | (68)<br>(69) |
| 473 | $1.78\times10^{-2}$ | $1.65\times10^{-2}$<br>$1.72\times10^{-2}$ | (68)<br>(69) |
| 498 | $0.989\times10^{-2}$ | $1.07\times10^{-2}$<br>$0.984\times10^{-2}$ | (68)<br>(69) |
| 523 | $5.83\times10^{-3}$ | $6.7\times10^{-3}$<br>$6.28\times10^{-3}$ | (68)<br>(69) |
| 548 | $3.61\times10^{-3}$ | $3.83\times10^{-3}$ | (69) |
| 593 | $1.68\times10^{-3}$ | $1.87\times10^{-3}$ | (70) |
| 623 | $1.07\times10^{-3}$ | $1.49\times10^{-3}$ | (70) |
| 651 | $.736\times10^{-3}$ | $1.26\times10^{-3}$ | (70) |

*(63) H. M. Stanley, J. E. Youell, J. B. Dymock, (64) M. P. Appleby, J. V. S. Glass, G. F. Horsley, (65) R. H. Bliss, B. F. Dodge.

$$C_2H_4 + C_2H_2 \rightleftharpoons C_4H_6 \text{ (1, 3-butadiene)}$$

The reaction forming butadiene from ethylene and acetylene in equimolar proportion was reported in 1866 by Berthelot [66] and has been studied recently by Naragon, Burk, and Lankelma [67], who conclude that acetylene in the absence of catalysts reacts more readily with ethylene than ethylene does with itself. As acetylene is so reactive, other reactions also occur, leading to products of higher molecular weight. Considering that the equilibrium constant for the formation of butadiene from ethylene and acetylene is very favorable at low and moderate temperatures, a catalyst specific for this reaction is desirable [68].

# XV. Comments on Cracking Reactions

The law of mass action and tables of equilibrium constants for different temperatures are helpful in the analysis of data on the products of cracking and condensation reactions of hydrocarbons. Thus tables of equilibrium constants show how, with increase of temperature, the equilibrium concentrations of unsaturated hydrocarbons increase with respect to the saturated hydrocarbons. The law of mass action determines the expected rate of increase in the relative equilibrium concentration of saturated hydrocarbons with increase of pressure. Besides depending upon temperature and pressure, the relative equilibrium concentrations of saturated and unsaturated hydrocarbons formed



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by cracking and condensation reactions are dependent upon the carbon to hydrogen ratio of the starting material, assuming no deposition of free carbon. The higher the carbon to hydrogen ratio, the greater the relative equilibrium concentration of the unsaturated hydrocarbons.

Two investigations of the products of the thermal cracking of hexane, one at high [69] and the other at low pressure [70], illustrate in a striking manner the influence of changes of pressure upon equilibrium concentrations. Thus at a pressure of 1,000 atmospheres and at temperatures of 783° K, there was no measurable concentration of hydrogen or any unsaturated hydrocarbon, whereas at a pressure of 0.18 atmosphere and 698° K the concentration of the unsaturated hydrocarbons exceeded that of the saturated compounds. In low pressure cracking reactions, equilibrium is approached from the side of low concentration of unsaturates, and in high pressure cracking from the side of high concentration of unsaturates.

The establishment of approximate equilibrium concentrations of hydrocarbons at temperatures of 700° to 800° K in the absence of catalysts requires times of the order of several hours. Thus in the products of a cracking process at high pressures [69] involving several reactions, one finds that the ratio $P[C_2H_4]\cdot P[H_2]/P[C_2H_6]$ changes from about 0.75 atmosphere to about 0.03 atmosphere during a period of about 2 hours at temperatures of 730° K. The equilibrium value is about $10^{-3}$ atmosphere. When several reactions occur in succession, the slowest reaction controls the approach to final equilibrium. For the most rapid reaction the apparent equilibrium constant as calculated from experimental compositions approaches the theoretical value relatively soon even though general equilibrium is not y attained, so that the individual composition continue to change. In cracking gas oil 1,223° K [71] and 0.23 atmosphere, the propo tions of $C_4H_6$, $H_2$, and $C_2H_4$ after a "conta time" of 0.05 second are fairly consistent wi the equilibrium constant for the reaction $2C_2H_4$ $C_4H_6+H_2$ as given in table 27, whereas the pr portions of butanes, butenes, butadiene, ethylen ethane, and hydrogen were not yet in approxima agreement with equilibrium constants for simp dehydrogenation reactions. On the other han the compositions obtained in the cracking isobutane [72], probably at about atmospher pressure, near 873° K and 923° K indicate valu of $P[C_4H_6]\cdot P[H_2]/P^2[C_2H_4]$ that differ from the ca culated values of the equilibrium constant b factors of the order of 100 after contact times the order of a minute and of several seconds, r spectively. In both cases these experiment values were changing with time. The well-know strong dependence of reaction rate on temperatu is particularly evident in this case. The rates many of these reactions double for each 15 to 2 degrees centigrade rise in temperature. Co relations of data for reaction rates for the therm decomposition of several hydrocarbons will b found in a review paper by Steacie [73] and discussion of the prediction of reaction rates i given in a paper by Daniels [74]. Numerou papers by Eyring and co-authors treat the subje of reaction rates, considering details of the struc ture of the activated complex, the configuratio of highest energy which the reacting molecule must have in changing from reactants to product of a reaction [75].

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# Effect of Catalysts and pH on Strength of Resin-Bonded Plywood[1]

*y Gordon M. Kline, Frank W. Reinhart, Royden C. Rinker, and Nicholas J. DeLollis*

The effects of various catalysts used to cure the resinous adhesives on the strength properties of plywood were investigated, particularly with regard to the degree of acidity developed by the catalysts in the resin film and in the plywood. The flexural, impact, and shear strengths, both initially and after aging, of birch plywoods bonded with urea-formaldehyde and phenol-formaldehyde resins definitely decrease as the acidity of the plywood increases, as evidenced by a decrease in pH. Only in the case of plywood bonded with casein and urea-formaldehyde resins had the deterioration at the bond progressed sufficiently in the roof-aging tests to make it impossible to carry out strength tests because of delamination. A correlation between decrease in strength on aging of plywood bonded with alkali-catalyzed phenolic acid and increase in alkalinity of the panel was observed. Because of the different absorption capacities of the phenolic resins for acids and alkalies, it is not possible to predict the pH of the plywood panel from the pH of the resin film.

The susceptibility of birch wood, itself, to attack by acids and alkalies was determined in order to better understand the mechanism of the deterioration of resin-bonded plywood. A marked decrease in strength occurred when the pH of the wood was lowered below 2.0. In the range between pH 2.0 and 2.5, strong acids, such as hydrochloric and sulfuric, had a more pronounced deteriorating effect than weak acids, such as hypophosphorous and nitranilic. A marked decrease in strength of the birch also occurred when the pH was raised to 8.8 by the absorption of an alkali, tetraethanolammonium hydroxide.

## I. Introduction

The increased use of resin-bonded plywood for tructural parts of aircraft has made it necessary o determine the effect of various chemical propties of the resins on the strength properties of he resin bonds. Information of this nature is eeded to utilize the materials properly in building atisfactory aircraft and to evaluate the causes of ailure. Determination of the effect of acid and lkaline catalysts on the strength and aging propties of various types of resin bonds is one imortant phase of this work. This report presents he results of an investigation which was made to etermine these relationships. Some of the data btained in the early stages of the work were ncluded in a preliminary report issued in 1943 [1].[2]

The degree of acidity or hydrogen-ion concenration can conveniently be reported as a pH

[1] NACA Technical Note No. 1161.
[2] Figures in brackets indicate the literature references at the end of this aper.

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value which approximately is the logarithm of the reciprocal of the gram ionic hydrogen equivalents per liter; that is, $pH = \log 1/H^+$ per liter. Water has a concentration of $H^+$ ion of $10^{-7}$ and of $OH^-$ ion of $10^{-7}$ moles per liter or a pH value of 7, and is said to be neutral in reaction. The presence of an acid in a water solution increases the concentration of hydrogen ions. Hence the concentration of hydrogen ions in an acid solution becomes $10^{-6}$ or $10^{-5}$, or greater, and the pH value is less than 7. The presence of an alkali in a water solution increases the concentration of hydroxyl ions and decreases that of the hydrogen ions. Hence the concentration of hydrogen ions in an alkaline solution becomes $10^{-8}$, $10^{-9}$, or less, and the pH value is greater than 7. The product of the hydrogen ion concentration and the hydroxyl-ion concentration is always equal to $10^{-14}$ in aqueous medium at 25° C. The pH value has been used throughout this report to indicate the degree of acidity of the various specimens.

The two most commonly used types of bonding agents in the manufacture of resin-bonded plywood are the phenol-formaldehyde and the urea-formaldehyde resins. Both types are cured either by the "hot-set" or the "cold-set" method. Since the demarcation between "cold-set" and "hot-set" bonding resins has not been definitely established in the industry, the resins used in this project were classified according to the temperature required to cure the resin in a commercially practical period of time, as follows:

*Class R.*—These resins do not require a higher degree of heat for curing than that available ordinary room or factory conditions.

*Class M.*—These resins require a degree of he greater than that available at room or facto conditions, but not over 160° F (71° C).

*Class H.*—These resins require a temperatu greater than 160° F (71° C).

To obtain a satisfactory degree of cure of class and some class *M* resins, it is necessary with mo of the commercial resins to use very active ca lysts. One of the most active catalysts for curi these types of resins is the hydrogen ion, which usually expressed in terms of pH units when th concentration is less than 1 molar.

It is an established fact that wood deteriorat rapidly in acidic media. It is also known th urea-formaldehyde resins are not as resistant acid condition as are phenolic resins [2–7]. Th work reported herein was designed to determi the effects of various catalysts and the pH of th resin bond on the strength properties of the resi wood composite since the failures may be in th resin, in the wood, or in both resin and wood. It should be noted, however, that the acid condi tions in the resin-bonded birch panels tested a attributable to the ingredients in the resin-glu mixtures and not to the wood or any extraneou source.

This investigation, conducted at the Nation Bureau of Standards, was sponsored by and co ducted with financial assistance from the Nation Advisory Committee for Aeronautics.

## II. Materials

A group of adhesives which are being used to a great extent in the manufacture of resin-bonded plywood aircraft was selected for this work. These included urea-formaldehyde, phenol-formaldehyde, resorcinol-formaldehyde, furane, and unsaturated polyester resins and casein. The commercial designations and the manufacturers of the resins, and the classification of the various resins and resin-catalyst mixtures on the basis of the temperature required for curing, are given in table 1.

Birch wood was used in the tests because it is the type most commonly employed in the manufacture of aircraft grade plywood in this country. Other woods were not investigated inasmuch as the primary objective of the investigation was the study of deteriorative effects characteristic various resin-catalyst systems.

The test panels were made with sliced bir veneers carefully selected for straightness of grai and having an average thickness of 0.01 in. Th thin veneers were used to obtain a higher resi content than that normally used in aircraft ply wood. As the acidic conditions result from th resin, a high resin content would be expected t magnify the effect of the pH on the strengt properties of the composite.

For the tests on the effect of the catalysts o the wood alone, sliced birch veneers 0.1 in. i thickness and specially selected for straightness o grain were used.

TABLE 1.—*Description of resins and resin-bonded birch panels*

| Commercial designation of resin | Manufacturer | Catalyst added to resin | Classification * | Conditions of cure | | Density, average | Resin content of panels, average | pH | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Temperature | Time | | | Resin film | Resin-bonded birch plywood | | | |
| | | | | | | | | | Unaged | Oven-aged | Oven-fog-aged | Roof-aged |
| **UREA-FORMALDEHYDE RESINS** | | | | | | | | | | | | |
| | | | | °F | hr : min | g/cm³ | Percent | | | | | |
| Permite 430 | Resinous Products and Chemical Co. | 10% Ammonium chloride. | R | Room | 24 : 00 | 0.91 | 33 | 1.2 | 1.9 | | | |
| Do | do | 10% "Z" | R | do | 24 : 00 | .91 | 37 | 1.6 | 2.0 | 2.1 | 2.6 | |
| Do | do | 10% "Y" | R | do | 24 : 00 | .94 | 40 | 1.8 | 2.4 | 2.5 | 3.3 | |
| Plaskon 201-2 | Plaskon Div., Libbey-Owens-Ford Glass Co. | 2% "A" | R | do | 24 : 00 | .93 | 37 | 2.6 | 3.2 | 3.4 | 3.3 | 3.9 |
| Casco 5 | Casein Company of America | 5% "AA" | R | do | 24 : 00 | 1.02 | 37 | 3.2 | 3.4 | 3.1 | 3.6 | |
| Plaskon 250-2 | Plaskon Div., Libbey-Owens-Ford Glass Co. | Incorporated with resin. | R | do | 24 : 00 | 0.88 | 34 | 3.4 | 3.6 | 3.4 | 3.6 | 3.8 |
| Plaskon 107 | do | 7% B-7 | H | 300 | 0 : 8 | .96 | 31 | 4.0 | 3.8 | 4.0 | 4.0 | 4.5 |
| Permite 500 | Resinous Products and Chemical Co. | None | H | 300 | 0 : 15 | .95 | 33 | 7.2 | 5.5 | 5.2 | 5.3 | 4.4 |
| Casco 5 | Casein Company of America | do | H | 300 | 0 : 30 | .98 | 35 | 7.5 | 5.7 | 6.0 | 5.9 | 3.9 |
| Permite 430 | Resinous Products and Chemical Co. | do | H | 300 | 0 : 6 | 1.00 | 33 | 7.7 | 4.6 | 4.6 | 4.7 | 3.6 |
| **UREA-RESORCINOL-FORMALDEHYDE RESINS** | | | | | | | | | | | | |
| Permite 500 | Resinous Products and Chemical Co. | 20% Q 107; 0.7% Q 87 | M | 150 | 3 : 00 | 0.99 | 35 | 2.9 | 5.1 | 4.2 | 4.7 | 4.0 |
| Plaskon 700-2 | Plaskon Div., Libbey-Owens-Ford Glass Co. | 10% Modifier | M | Room<br>150 | 20 : 00<br>3 : 00 | .96 | 35 | 4.8 | 4.6 | 4.6 | 4.6 | 4.1 |
| **PHENOL-FORMALDEHYDE RESINS** | | | | | | | | | | | | |
| Durez 12041 | Durez Plastics and Chemicals, Inc. | 10% 7422 | M | 150 | 24 : 00 | 0.97 | 36 | 1.4 | 1.8 | 1.8 | 1.9 | 2.6 |
| Durez 11427 | do | 10% 7422 | M | 150 | 24 : 00 | 1.04 | 39 | 1.4 | 1.8 | 1.8 | 1.9 | 2.6 |
| Catabond 590 | Catalin Corp | 11% Hydrochloric acid (27.8%). | M | Room<br>150 | 24 : 00<br>1 : 00 | 0.90 | 37 | 1.6 | 1.7 | 2.0 | 2.3 | 3.1 |
| Catabond 200 CZ | do | do | M | Room<br>150 | 24 : 00<br>1 : 00 | .91 | 37 | 1.6 | 1.8 | 2.1 | 2.4 | 2.8 |
| Bakelite XC-3931 | Bakelite Corp | 3% XK-2007 | M | Room<br>150 | 24 : 00<br>2 : 00 | .90 | 31 | 1.9 | 2.7 | 2.8 | 3.0 | 3.3 |
| Bakelite XC-11749 | do | 45% XK-11753 | R | Room | 24 : 00 | .87 | 31 | 1.9 | 3.1 | 3.0 | 3.3 | 3.3 |
| Catabond 590 | Catalin Corp | None | H | 300 | 0 : 30 | .94 | 29 | 3.8 | 3.6 | 3.7 | 3.6 | 3.4 |
| Bakelite XC-3931 | Bakelite Corp | do | H | 300 | 0 : 30 | .97 | 35 | 5.5 | 4.5 | 4.7 | 4.5 | 3.5 |
| Bakelite XC-11749 | do | do | H | 300 | 0 : 45 | .93 | 42 | 5.9 | 3.9 | 3.9 | 3.9 | 3.7 |
| Catabond 200 CZ | Catalin Corp | do | H | 300 | 0 : 30 | 1.00 | 31 | 6.6 | 4.6 | 4.6 | 4.7 | 4.3 |
| Cascophen LT-67 | Casein Company of America | 8% M-18 | M | 150 | 24 : 00 | 0.95 | 37 | 7.5 | 6.4 | 6.2 | 6.2 | 5.0 |
| Durez 12041 | Durez Plastics and Chemicals, Inc. | None | H | 300 | 0 : 30 | .97 | 33 | 8.2 | 5.0 | 5.0 | 5.0 | 4.6 |
| Bakelite BC-17540 | Bakelite Corp | 15% BC-17545 | M | 150 | 24 : 00 | .94 | 21 | 9.2 | 7.3 | | 7.3 | |
| Tego film | Resinous Products and Chemical Co. | None | H | 300 | 0 : 10 | .80 | 20 | 9.5 | 8.2 | | | |
| Amberlite PR-14 | do | Incorporated with resin. | H | 300 | 0 : 12 | .85 | 23 | 9.8 | 8.4 | 8.3 | 8.0 | 6.2 |
| **RESORCINOL-FORMALDEHYDE RESINS** | | | | | | | | | | | | |
| Durez 12490 | Durez Plastics and Chemicals, Inc. | 30% Formaldehyde (37%). | R | Room | 24 : 00 | 0.81 | 26 | 5.7 | 4.8 | 5.2 | 5.3 | 4.9 |
| Penacolite G-1131 | Pennsylvania Coal Products Co. | 20% G-1131 B | R | do | 24 : 00 | .89 | 26 | 6.0 | 5.1 | | 5.2 | 4.1 |
| Bakelite XC-17613 | Bakelite Corp | 20% XK-17618 | M | 150 | 24 : 00 | .97 | 28 | 6.2 | 4.8 | | 4.6 | |
| Amberlite PR-75 B | Resinous Products and Chemical Co. | 22% P-79 | M | 150 | 24 : 00 | .94 | 32 | 6.4 | 5.4 | | 4.8 | |
| Penacolite G-1124 | Pennsylvania Coal Products Co. | 25% G-1124-B | R | Room | 24 : 00 | .94 | 33 | 7.0 | 5.1 | 5.2 | 5.4 | 4.5 |
| Durite S-3026 | Durite Plastics, Inc. | 16% 3026A | R | do | 24 : 00 | .86 | 22 | 7.5 | 6.3 | | 6.0 | |

See footnote at end of table.

TABLE 1.—*Description of resins and resin-bonded birch panels*—Continued

| Commercial designation of resin | Manufacturer | Catalyst added to resin | Classification [a] | Conditions of cure | | Density, average | Resin content of panels, average | pH | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Temperature | Time | | | Resin film | Resin-bonded birch plywood | | | |
| | | | | | | | | | Unaged | Oven-aged | Oven-fog-aged | Ra... aged |
| **PHENOL-RESORCINOL-FORMALDEHYDE RESIN** | | | | | | | | | | | | |
| | | | | °F | *hr : min* | *g/cm³* | *Percent* | | | | | |
| Durez 12533 | Durez Plastics and Chemicals, Inc. | 100% 12534 B | *M* | 150 | 24 : 00 | 0.94 | 38 | 6.6 | 5.1 | 5.5 | 5.4 | 5... |
| **FURANE RESIN** | | | | | | | | | | | | |
| Resin X | Plastics Industries Technical Institute. | 5% Z-1A | *R* | Room | 24 : 00 | 1.00 | 28 | 1.7 | 2.2 | ..... | 2.3 | 2... |
| **CASEIN GLUE** | | | | | | | | | | | | |
| Aircraft joint P glue | Casein Company of America | None | *R* | Room | 24 : 00 | 0.88 | 34 | 12.0 | 8.4 | 7.8 | 8.0 | ... |
| **UNSATURATED POLYESTER RESINS** | | | | | | | | | | | | |
| Laminac | American Cyanamid Co | 1% Benzoyl Peroxide | *H* | 125 | 0 : 30 | 0.83 | 26 | 2.4 | 5.7 | 3.9 | 3.8 | 1... |
| | | | | 300 | 0 : 5 | | | | | | | |
| Do | do | 1% Lauroyl Peroxide | *H* | 125 | 0 : 30 | .81 | 24 | 2.8 | 4.0 | 4.0 | 4.0 | 1... |
| | | | | 300 | 0 : 5 | | | | | | | |
| MR-17-A2 | Marco Chemical Co | 3% Benzoyl Peroxide | *H* | 230 | 2 : 00 | 1.05 | 41 | 3.2 | 3.7 | 3.9 | 2.7 | 1... |
| MR-17-B1 | do | do | *H* | 230 | 2 : 00 | 1.01 | 39 | 3.4 | 3.2 | 3.3 | 2.8 | 1... |
| Plaskon 900 | Plaskon Div., Libbey-Owens-Ford Glass Co. | 2% Benzoyl Peroxide | *M* | 150 | 24 : 00 | 0.94 | 29 | 3.3 | 3.8 | ..... | 3.4 | ... |
| CR-39 | Pittsburgh Plate Glass Co | 5% Benzoyl Peroxide | *H* | 160 | 72 : 00 | 1.21 | 51 | 5.1 | 3.9 | 2.7 | 2.7 | 1... |

[a] The resins are classified according to the temperature required to cure the resin. Class *R* includes those which cure quickly at room temperature. Class *M* includes those which require a temperature above room temperature but not over 160° F. to cure. Class *H* includes those which require a temperature above 160° F. to cure.

# III. Preparation of Test Panels

The resin glues were prepared according to directions received from the manufacturers and were applied to the birch veneers by means of rollers. This method produced resin films of uniform thickness on both sides of the veneers. The veneers coated with the class *H* resins were suspended from a drying rack and allowed to dry about 20 hours before the assembling and pressing. The veneers coated with the class *R* and class *M* resins were assembled and pressed immediately after coating. Each panel consisted of eight birch veneers arranged with the grain of plies one, three, six, and eight parallel to one another and with the grain of plies two, four, five, and seven perpendicular to the face plies.

In the early stages of the investigation the test panels were pressed at approximately 100 lb/in.², but this produced panels varying considerably in thickness and density. To obtain more uniform panels, stops 9 by 1 in. for use between the press platens were ground to a thickness of 0.075±0.001 in., and the platens were ground to a flatness of 0.0001 in. A load of 10 tons was applied to the platens.

The birch veneers used in each panel were conditioned by storage at 77° F (25° C) and 50-percent relative humidity, and were weighed before the resin coating was applied. The completed test panel was also conditioned and weighed. The resin content (in percent) of the test panel was then calculated by means of the equation

$$\frac{\text{wt of test panel} - \text{wt of conditioned veneers}}{\text{wt of test panel}} \times 100.$$

Three panels were prepared with each resin or resin-catalyst mixture. The conditions used to cure the panels, the average densities, and the average resin contents are given in table 1.

# IV. Testing Procedures

## 1. Aging

Each test panel was cut into quarters and ated as follows:

One quarter section was not subjected to any ing treatment.

One quarter section was exposed continuously in ashington, D. C., (on the roof of the Industrial ilding, National Bureau of Standards) on racks an angle of 45°, facing south for 1 year unless herwise noted.

One quarter section was heated in a forced-draft en at 176° F (80° C) for 40 hours.

One quarter section was subjected to a continuus oven-fog cyclic accelerated aging test. The rcle in this test consisted of the following:

| Exposure period | Temperature | | Relative humidity | Apparatus |
|---|---|---|---|---|
| *hr* | *°F* | *°C* | *Percent* | |
| | 77 | 25 | 100 | Fog cabinet. |
| | 149 | 65 | 5 | Forced-draft oven. |
| | 77 | 25 | 100 | Fog cabinet. |
| | 149 | 65 | 5 | Forced-draft oven. |

he sections were exposed for a total of 200 ours in the oven and 40 hours in the fog cabinet. This latter test is a modification of the accelerted weathering test described in Federal Specication L–P–406a, Method 6021. Heating in an ven at 149° F (65° C) was substituted for the radiation under the sunlamp prescribed in Method 6021 because the effect of the ultraviolet ght would be expected to be negligible in the reakdown of the resin layer in plywood. The emperature to which the specimens are exposed approximately 149° F (65° C) in both tests. The data in table 2 show that the decreases in flexural strength resulting from exposure of plywood specimens to the two tests, respectively, are practically identical.

## 2. Determination of pH

A thin film of the resins of class R and class M was cast on glass and allowed to dry for 20 hours at a temperature of 70° to 79° F (21° to 26° C). The resin film was then removed from the glass and ground to a fineness of 40 mesh. Two grams of the powdered resin were suspended in 10 milliliters of distilled water and the pH of the suspension was measured by means of a glass electrode after 15 minutes, and after 24, 48, 72, and 96 hours, or until the values were constant to within 0.05 pH unit.

Films were prepared from the class H resins by casting them upon a glass plate, using a knife blade to remove excess resin and make the thickness of the coating 0.02 in. or less. The cast films were placed in a circulating-air oven at 149° F (65° C) until examination showed that most of the solvent had evaporated; this process required about 4 hours except in the case of Plaskon 107, which was cured after 3 hours at 149° F (65° C) and was not subjected to any further heating. This drying was followed by a cure in the oven at 300° F (149° C) until the films were hard and brittle, the latter operation requiring about 30 minutes. The hard, brittle films were pulverized in a small rock-crushing mortar and passed through a 40-mesh screen. The pH values of the powdered films were measured in the same manner as those of the class *R* and the class *M* films.

TABLE 2.—*Effect of oven-fog and sunlamp-fog aging tests (240 hours) on flexural strength of resin-bonded birch plywood panels*

| Commercial designation of resin | Catalyst added to resin | Unaged panel | | Oven-fog-aged panel | | Sunlamp-fog-aged panel | |
|---|---|---|---|---|---|---|---|
| | | Average pH | Flexural strength | Flexural strength | Loss due to aging | Flexural strength | Loss due to aging |
| | | | *lb/in.²* | *lb/in.²* | *Percent* | *lb/in.²* | *Percent* |
| kelite XC–11749 | None | 4.8 | 27,600 | 22,200 | 19.6 | 21,900 | 20.6 |
| Do | 45% XK–11753 | 3.1 | 20,500 | 16,300 | 18.0 | 15,300 | 25.4 |
| tabond 590 | None | 3.5 | 28,100 | 21,700 | 22.8 | 22,100 | 21.4 |
| Do | 11% hydrochloric acid (27.8%) | 1.8 | 15,600 | 10,800 | 30.8 | 11,000 | 29.5 |
| rmite 500 | None | 6.7 | 23,000 | 19,100 | 17.0 | 18,600 | 19.1 |
| Do | 10% ammonium chloride | 1.8 | 14,800 | 7,900 | 46.6 | 6,700 | 54.7 |

The acidity of the test panels was determined by grinding a portion of the panel to 40 mesh in a Wiley mill and suspending 1 g of the powder in 5 ml of distilled water. The pH values of the water suspensions were usually constant after 48 hours.

The pH of the distilled water used in making the resin suspensions was 6.3. A few of the resin films and powdered panels were also suspended in dilute hydrochloric acid solution of pH 4.5. The pH values of the acid suspensions are reported in table 2 and do not differ appreciably from those of the water suspensions. All the pH measurements were made at a temperature of 77° F (25° C) with a glass electrode. The measurements reported are accurate to ±0.05 pH unit.

## 3. Strength Properties

The test specimens for determining the strength properties were cut from the quarter sections after the aging treatments. The specimens were machined and then conditioned at 77° F (25° C) and 50-percent relative humidity for at least 48 hours prior to testing. All the tests were made at 77° F (25° C) and 50-percent relative humidity.

The flexural modulus of elasticity was measured on an Olsen Stiffness Tester, Tour-Marshall design. Specimens 5 in. long and 0.5 in. wide were cut from the panels. Two measurements were made on each specimen, one on each end. The test span was 2 in. long; the total bending moment applied to the specimen was 3 in.-lb. The angular deflections were plotted against the bending moments and the deflection at a stress of 2,500 lb/in.$^2$ was determined from the curve. A stress of 2,500 lb/in.$^2$ was selected because the plots for all the samples were essentially straight lines up to that stress. The secant modulus of elasticity in flexure then was calculated from the approximate expression,

$$E=\frac{229.2PL^3}{Dah^3}, \qquad (1)$$

where

$E$=modulus of elasticity in flexure
$P$=load
$L$=length of beam
$D$=deflection, degrees
$a$=width of beam, and
$h$=thickness of beam.

This expression was derived from the formula f the deflection of a cantilever beam with a concen trated load at one end.

The flexural strength was measured on spec mens 1.0 in. long and 0.75 in. wide cut from t panels. The specimen was supported on tw parallel supports with a span of ⅝ in. The loa was applied at the center of the span by a pressur piece similar to the supports. The edges of th support pieces and of the pressure piece we rounded to ⅛-in. radius. The tests were made on hydraulic testing machine with a head speed 0.05 in./min. The machine was accurate to percent of the lowest applied load. The flexur strength or modulus of rupture is calculated fro the expression

$$F=\frac{3PL}{2ah^2}, \qquad (2$$

where $F$ is flexural strength, and the other sym bols have the same significance as in eq. 1.

The impact tests were made on an Izod impac machine of 2 ft-lb capacity. Specimens 2.5 in long and 0.5 in. wide were cut from the panels.

The tensile tests were made according to Metho 1011 of Federal Specification L–P–406. Type specimens were used; the width of the reduce section was 0.5 in. The tests were made on hydraulic testing machine with self-aligning Temp lin grips. The rate of head speed was 0.05 in./min

Shear specimens 4 in. long and 0.75 in. wide we cut from the panels. A groove ⅛ in. wide an extending through approximately 4½ veneers wa milled on one face of the panel parallel to th 0.75-in. dimension. A similar groove was mille on the opposite face. The grooves on the spec mens used in the preliminary tests were ½ in apart, but, as many tensile failures were obtained the distance between the grooves was reduced t ¼ in. on the later specimens. The specimens were broken on a hydraulic testing machine at a rat of loading of 200 lb/in.$^2$ per minute.

## 4. Delamination

One strip 0.5 in. wide cut from each quarter section of each test panel was subjected to a delam ination test. The strips were placed in individual 3- by 20-centimeter test tubes that contained distilled water previously heated to the boiling point by immersion of the tubes in a water bath. The tubes containing the test strips were left in

e bath of boiling water for 1 hour. On removal m the test tubes the specimens were immersed water at 77° F (25° C) for 15 minutes and en dried at 140° F (60° C) in a forced-draft en for 22 hours. This procedure constituted e cycle of the test. At the end of each cycle the t specimens were bent over a mandrel of 8-in. radius. After five cycles the specimens were bent over a 4-in. radius mandrel. Observations regarding delamination were made.

### 5. Density

Density was determined by weighing and measuring machined specimens.

## V. Results of Tests

A preliminary investigation was made to obtain ta for use in selecting the strength properties be measured on all the test panels. Six panels re prepared with a phenol-formaldehyde resin ego film) and six with a urea-formaldehyde in (Uformite 430 catalyzed with 10-percent monium chloride). These two materials were lected to determine the effects of high and low H conditions respectively. Specimens from each nel were tested unaged and after exposure to ree aging tests. The strength properties meas- ed in these preliminary tests were flexural odulus of elasticity, and flexural, impact, tensile, d shear strengths. The changes in these strength roperties as a result of exposure to the aging nditions are given in table 3.

On the basis of the results obtained in these eliminary tests, the size of the test specimens quired, and an analysis of the stresses in the rious tests, it was decided to employ the flexural, pact, and shear strengths for detecting the de- rioration of the resin-bonded birch plywoods.

The detailed results of these tests are presented tables 4, 5, and 6 and figures 5 to 12, inclusive. he behavior of the materials with respect to elamination is shown in table 7. A summary of he effects of the catalysts on the strength proper- es of the panels bonded with urea-formaldehyde nd phenol-formaldehyde resins is given in table 8.

The specific effects of various acid and basic adicals in catalysts used with phenolic resinous dhesives in the preparation of plywood were etermined in a series of tests with known com- ounds. Panels were prepared with a resorcinol- ormaldehyde resin (Penacolite G–1131) to which as added varying amounts of hydrochloric, nitric, ulfuric, phosphoric, hypophosphorous, trichloro- cetic, benzenesulfonic, and nitranilic acids, and

TABLE 3.—*Changes in strength properties of birch plywoods caused by various aging methods*

| Panel designation | Change for panels bonded with phenolic resin (Tego film) | | | Change for panels bonded with urea-formaldehyde resin (Uformite 430 with 10-percent ammonium chloride catalyst) | | |
|---|---|---|---|---|---|---|
| | Oven-aged | Oven-fog-aged | Roof-aged 6 months | Oven-aged | Oven-fog-aged | Roof-aged 6 months |
| | TENSILE STRENGTH | | | | | |
| | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* |
| A | 0 | +3 | +7 | −14 | −21 | +19 |
| B | +7 | +6 | −11 | −22 | −4 | −42 |
| | FLEXURAL STRENGTH | | | | | |
| A | −6 | −1 | −7 | −15 | −41 | −53 |
| B | −12 | +3 | −5 | −10 | −51 | −72 |
| | SECANT FLEXURAL MODULUS OF ELASTICITY (0 TO 2,500 LB/IN.²) | | | | | |
| A | −25 | +12 | −23 | −15 | 0 | −18 |
| B | −18 | +17 | −13 | −25 | 0 | −2 |
| | IZOD IMPACT STRENGTH, FLATWISE | | | | | |
| A | +36 | +14 | −26 | −18 | −38 | −20 |
| B | 0 | −28 | +38 | −10 | −27 | +10 |
| | IZOD IMPACT STRENGTH, EDGEWISE | | | | | |
| A | +17 | −7 | +17 | −38 | −50 | +8 |
| B | −11 | −18 | −18 | −15 | −6 | +80 |
| | SHEAR STRENGTH | | | | | |
| A | +11 | −46 | −33 | −5 | −50 | −5 |
| B | −43 | +70 | −25 | +5 | −38 | ..... |

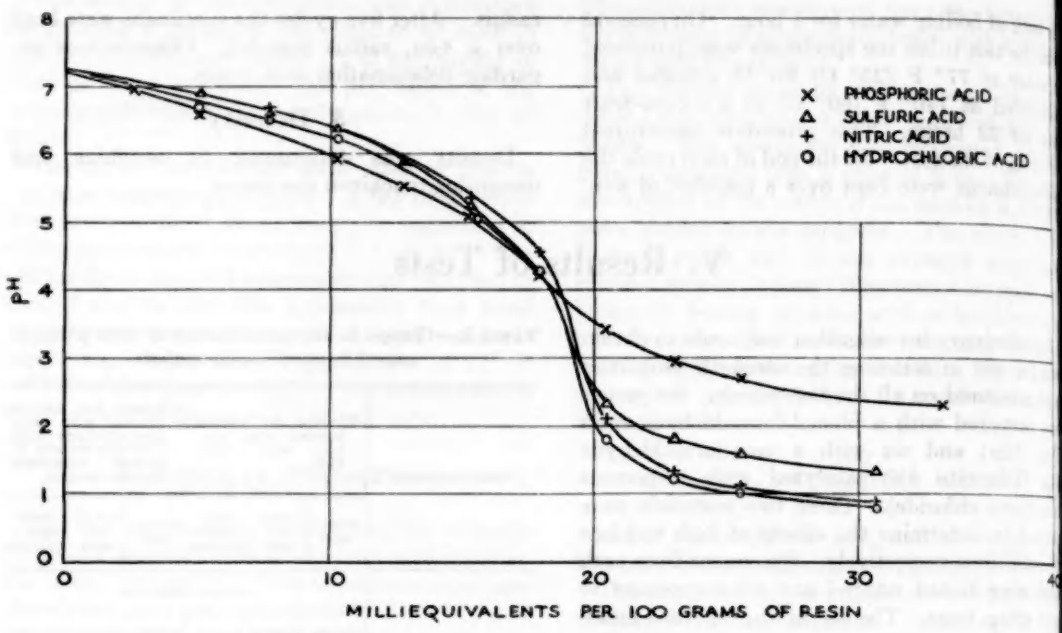



FIGURE 1.—*Titration of Penacolite G-1131 with various acids.*

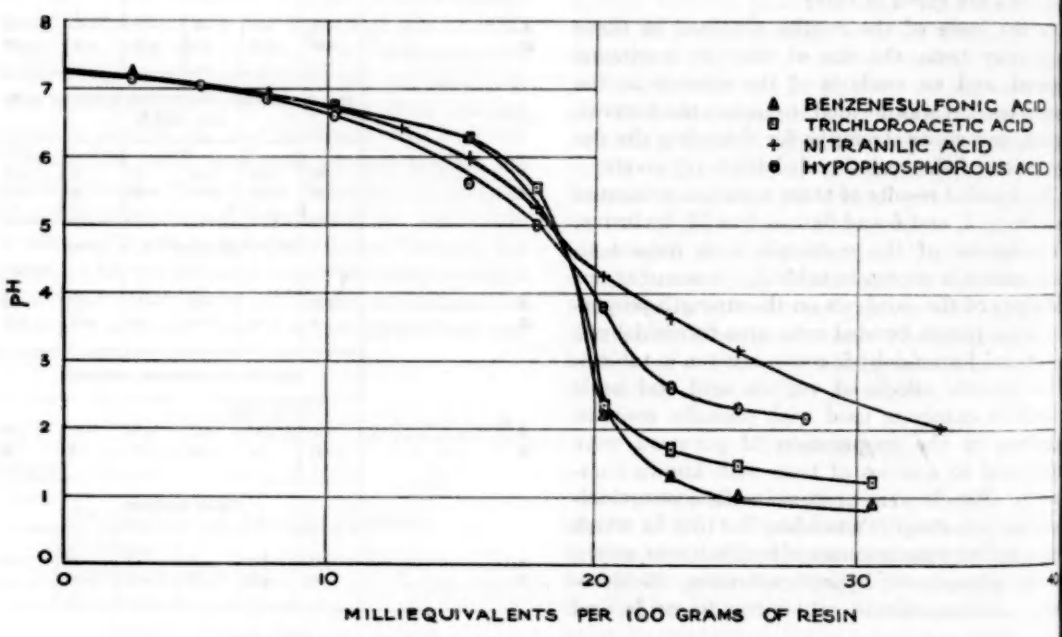



FIGURE 2.—*Titration of Penacolite G-1131 with various acids.*

odium hydroxide. Titration curves of the resin ith these acids and base are shown in figures 1, , and 3. The flexural strengths of these panels, naged and oven-fog-aged, are presented in table 9.

Similar experiments were performed with two henol-formaldehyde resins. The titration curves btained for one of these resins (Cascophen LT–67) ith the acids and base are shown in figures 3 and 4. he results of the strength tests are given in able 10.

In a further series of tests to determine the pecific effect of the acid radicals in commercial atalysts for resinous adhesives, three commercial atalysts were used, respectively, with three henolic resins to prepare plywood panels. Four anels were prepared with each resin—one without catalyst, and one with each of the three atalysts, respectively. Only one of the resin-atalyst mixtures failed to cure satisfactorily at 50°F (66°C). The flexural strengths of these anels were determined before and after aging. he results of these tests are presented in table 11. Data are also given in table 11 for one of the resin-atalyst mixtures in which the catalyst percentage as varied from 5 to 45 percent.

Proper interpretation of the data obtained in hese experiments on the effects of various acid nd alkaline catalysts on the strength of resin-onded plywood required information on the effects of these chemicals on the wood itself. Accordingly, birch veneers of 0.1-in. thickness were immersed for 3 days in various concentrations of he same acids and alkalies used in the tests with he resins. The results of flexural strength measurements on the conditioned wood specimens re shown in table 12.

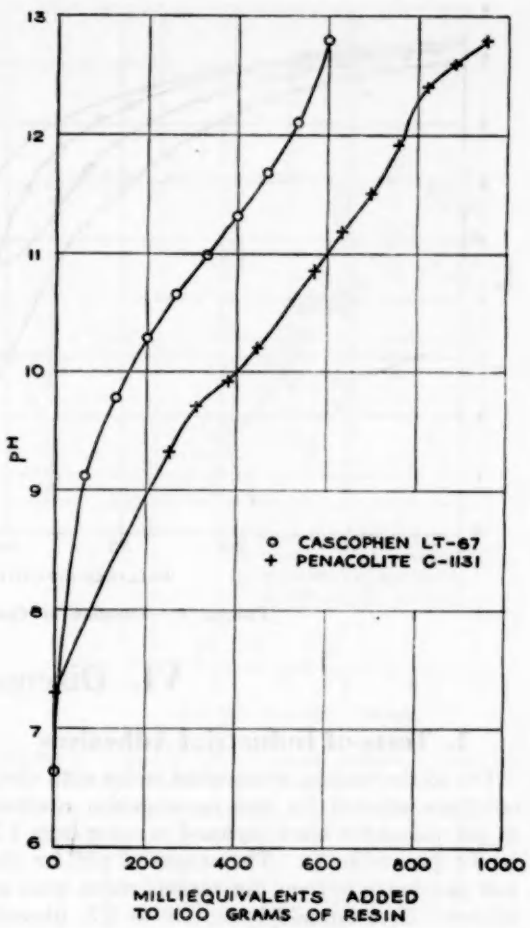



FIGURE 3.—*Titration of phenol and resorcinol resins with sodium hydroxide.*

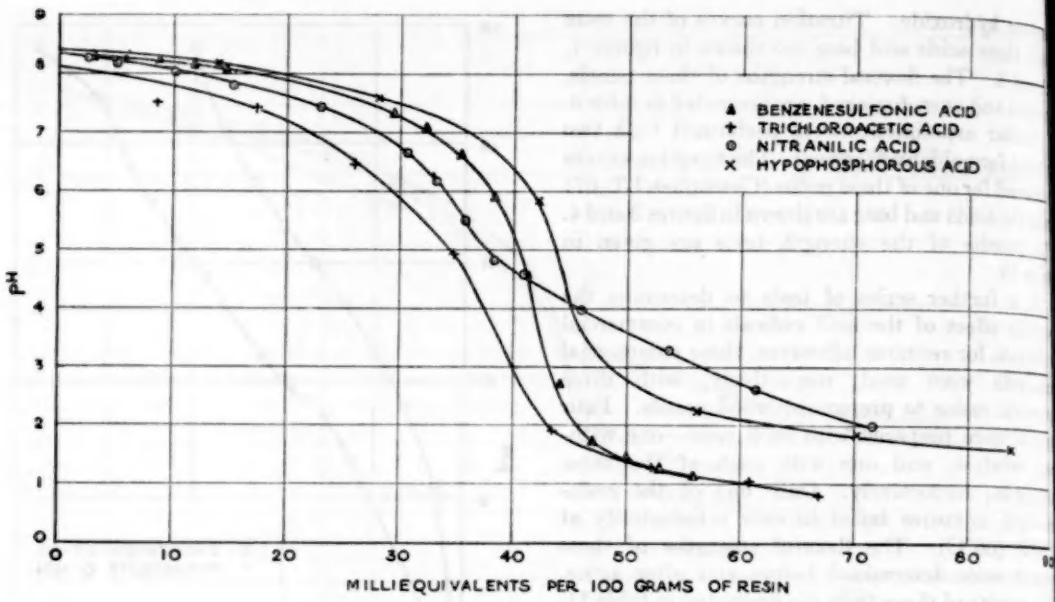



FIGURE 4.—*Titration of Cascophen LT–67 with various acids.*

# VI. Discussion of Results

## 1. Tests of Industrial Adhesives

Use of the various commercial resins with their catalysts selected for this investigation resulted in pH values for birch plywood ranging from 1.7 to 8.4 (see table 1). The ranges of pH for the test panels made from the various resins were as follows: Urea-formaldehyde, 1.9 to 5.7; phenol-formaldehyde, 1.7 to 8.4; resorcinol-formaldehyde, 4.8 to 6.3; and unsaturated polyester resins, 3.2 to 5.7.

The pH values of birch plywood were not affected by moderate baking or by exposure to cycles of heat and fog. This indicated that the acidic compounds determining the pH of the composite did not escape readily from the structure or did not react with the birch or its decomposition products in such a way that they lost their chemical identity. It would seem reasonable, therefore, to assume that the deterioration caused by pH would continue until failure occurred.

The results of the 240-hour oven-fog-aging te are in qualitative agreement with the results the 1-year roof-aging test. An analysis of th data indicates that no quantitative statement can be made concerning the agreement. How ever, the 1-year roof-aging test was usually, bu not always, more severe than the 240-hou oven-fog-aging test.

The effects of pH on the strength of the plywoo prepared with the various commercial types resins can best be reviewed by discussing the resi in the following three groups: Urea, phenolic, an other resins.

### (a) Urea Resins

The flexural, impact, and shear strengths of th urea-formaldehyde resin-bonded birch plywoo depended markedly on the pH of the composite This is shown by the data in tables 4, 5, and and graphically in figures 5, 6, and 7.

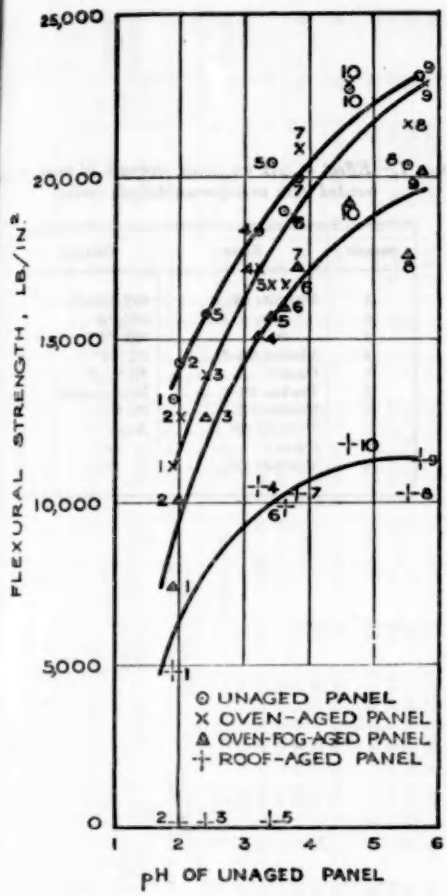



FIGURE 5.—*Effect of* pH *on flexural strength of birch plywood bonded with urea-formaldehyde resins.*

| Sample | Resin | Catalyst |
|---|---|---|
| 1 | Uformite 430 | 10% $NH_4Cl$. |
| 2 | do | 10% "*Z*". |
| 3 | do | 10% "*Y*". |
| 4 | Plaskon 201-2 | 2% "*A*". |
| 5 | Casco 5 | 5% "*A*". |
| 6 | Plaskon 250-2 | Incorporated. |
| 7 | Plaskon 107 | 7% B-7. |
| 8 | Uformite 500 | None. |
| 9 | Casco 5 | Do. |
| 10 | Uformite 430 | Do. |

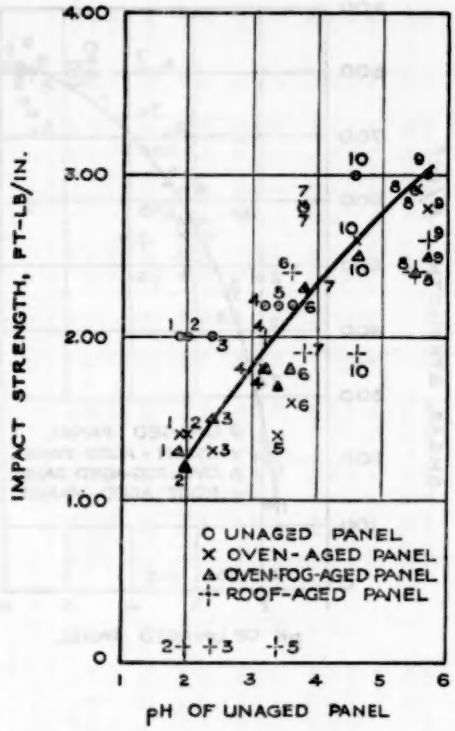



FIGURE 6.—*Effect of* pH *on impact strength of birch plywood bonded with urea-formaldehyde resins.*

| Sample | Resin | Catalyst |
|---|---|---|
| 1 | Uformite 430 | 10% $NH_4Cl$. |
| 2 | do | 10% "*Z*". |
| 3 | do | 10% "*Y*". |
| 4 | Plaskon 201-2 | 2% "*A*". |
| 5 | Casco 5 | 5% "*A*". |
| 6 | Plaskon 250-2 | Incorporated. |
| 7 | Plaskon 107 | 7% B-7. |
| 8 | Uformite 500 | None. |
| 9 | Casco 5 | Do. |
| 10 | Uformite 430 | Do. |

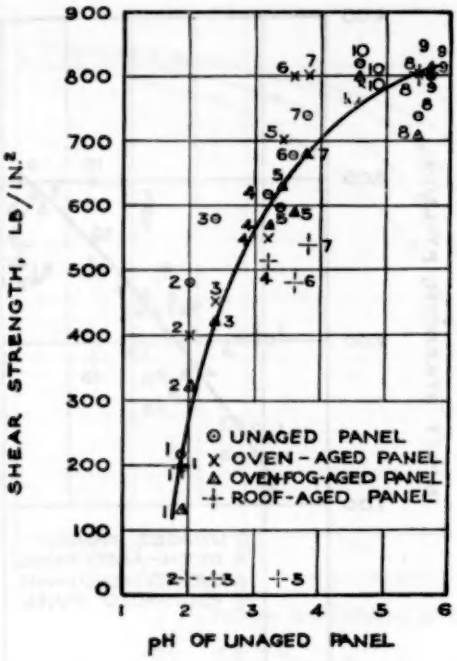



Figure 7.—*Effect of* pH *on shear strength of birch plywood bonded with urea-formaldehyde resins.*

| Sample | Resin | Catalyst |
|---|---|---|
| 1 | Uformite 430 | 10% $NH_4Cl$. |
| 2 | do | 10% "Z". |
| 3 | do | 10% "Y". |
| 4 | Plaskon 201-2 | 2% "A". |
| 5 | Casco 5 | 5% "AA". |
| 6 | Plaskon 250-2 | Incorporated. |
| 7 | Plaskon 107 | 7% B-7. |
| 8 | Uformite 500 | None. |
| 9 | Casco 5 | Do. |
| 10 | Uformite 430 | Do. |

TABLE 4.—*Effect of exterior use [illegible] on flexural strength of resin-bonded plywood*

| Commercial designation of resin | Catalyst added to resin | Classification | pH of unaged panel | Unaged panel: Flexural strength: Average | Unaged panel: Flexural strength: Range | Unaged panel: No. of specimens | Oven-aged panel: Flexural strength: Average | Oven-aged panel: Flexural strength: Range | Oven-aged panel: No. of specimens | Oven-aged panel: Change in strength | Oven-fog-aged panel: Flexural strength: Average | Oven-fog-aged panel: Flexural strength: Range | Oven-fog-aged panel: No. of specimens | Oven-fog-aged panel: Change in strength | Roof-aged panel: Flexural strength: Average | Roof-aged panel: Flexural strength: Range | Roof-aged panel: No. of specimens | Roof-aged panel: Change in strength |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Flexural strength data | | | | | | | | | | | | | | |
| | | | | | | | Oven-aged panel | | | | Oven-fog-aged panel | | | | Roof-aged panel | | | |
| | | | | Flexural strength | | | | | | | | | | | | | | |
| **UREA-FORMALDEHYDE RESINS** | | | | | | | | | | | | | | | | | | |
| | | | | *lb/in.²* | *lb/in.²* | | *lb/in.²* | *lb/in.²* | | *Percent* | *lb/in.²* | *lb/in.²* | | *Percent* | *lb/in.²* | *lb/in.²* | | *Percent* |
| Uformite 430 | 10% $NH_4Cl$ | *R* | 1.9 | 13,200 | 10,800 to 15,500 | 12 | 11,100 | 9,900 to 12,800 | 9 | −16 | 7,400 | 5,600 to 9,400 | 16 | −44 | 4,900[a] | 2,800 to 6,200 | 6 | −64 |
| Do | 10% "Z" | *R* | 2.0 | 14,300 | 11,300 to 15,600 | 12 | 12,600 | 11,100 to 15,000 | 12 | −12 | 10,100 | 7,800 to 12,200 | 12 | −29 | (*b*) | | | |
| Do | 10% "Y" | *R* | 2.4 | 15,800 | 14,600 to 17,400 | 12 | 13,900 | 11,500 to 15,600 | 11 | −12 | 12,600 | 9,600 to 14,200 | 11 | −20 | (*b*) | | | |
| Plaskon 201-2 | 2% "A" | *R* | 3.2 | 18,400 | 16,900 to 19,800 | 12 | 17,200 | 15,800 to 18,900 | 12 | −7 | 15,100 | 12,300 to 17,700 | 12 | −18 | 10,500 | 8,500 to 11,600 | 12 | −43 |
| Casco 5 | 5% "AA" | *R* | 3.4 | 20,500 | 18,800 to 22,300 | 12 | 16,700 | 13,400 to 19,700 | 11 | −19 | 15,700 | 12,200 to 20,700 | 12 | −23 | (*b*) | | | |
| Plaskon 250-2 | Incorporated with resin. | *R* | 3.6 | 19,000 | 17,100 to 19,600 | 12 | 16,700 | 12,800 to 19,600 | 12 | −12 | 16,000 | 15,200 to 17,700 | 12 | −16 | 9,900 | 8,400 to 11,400 | 12 | −48 |
| Plaskon 107 | 7% B-7 | *H* | 3.8 | 20,000 | 16,500 to 21,200 | 15 | 20,400 | 18,200 to 21,200 | 12 | +2 | 17,200 | 16,000 to 20,400 | 12 | −14 | 10,300 | 9,200 to 11,500 | 15 | −49 |
| Uformite 500 | None | *H* | 5.5 | 20,400 | 16,600 to 24,000 | 15 | 21,600 | 18,200 to 23,600 | 15 | +6 | 17,600 | 11,800 to 19,100 | 11 | −14 | 10,300 | 9,700 to 11,300 | 15 | −50 |
| Casco 5 | do | *H* | 5.7 | 23,100 | 19,300 to 26,600 | 13 | 23,000 | 19,600 to 25,600 | 15 | −0.4 | 21,200 | 16,600 to 26,700 | 13 | −8 | 11,300 | 8,000 to 13,700 | 15 | −51 |
| Uformite 430 | do | *H* | 4.6 | 22,700 | 20,700 to 25,700 | 15 | 22,800 | 19,500 to 27,400 | 15 | +0.4 | 19,200 | 17,000 to 24,100 | 15 | −15 | 11,800 | 5,800 to 13,900 | 15 | −48 |
| **UREA-RESORCINOL-FORMALDEHYDE RESINS** | | | | | | | | | | | | | | | | | | |
| Uformite 500 | 20% Q-107; 0.7% Q-87. | *M* | 5.1 | 19,100 | 16,400 to 22,500 | 12 | 21,400 | 17,800 to 25,400 | 12 | +12 | 20,800 | 18,500 to 23,700 | 12 | +9 | 11,000 | 9,000 to 12,400 | 12 | −43 |
| Plaskon 700-2 | 16% modifier | *M* | 4.6 | 21,800 | 20,500 to 23,400 | 12 | 22,900 | 20,300 to 25,700 | 12 | +5 | 21,300 | 15,900 to 24,800 | 12 | −2 | 16,000 | 14,000 to 18,000 | 12 | −27 |
| **PHENOL-FORMALDEHYDE RESINS** | | | | | | | | | | | | | | | | | | |
| Durez 12041 | 10% 7422 | *M* | 1.8 | 19,400 | 17,300 to 20,600 | 12 | 19,000 | 17,100 to 21,800 | 11 | −2 | 13,500 | 10,100 to 15,300 | 12 | −30 | 9,600 | 8,400 to 10,900 | 12 | −51 |
| Durez 11427 | 10% 7422 | *M* | 1.8 | 20,200 | 16,700 to 21,800 | 12 | 18,200 | 15,100 to 20,500 | 12 | −10 | 11,800 | 9,900 to 13,900 | 12 | −42 | 10,400 | 8,600 to 12,200 | 12 | −49 |
| Catabond 590 | 11% HCl acid (27.8%). | *M* | 1.7 | 10,500 | 6,800 to 12,700 | 12 | 11,100 | 8,700 to 12,500 | 12 | +5 | 9,300 | 7,800 to 11,600 | 12 | −11 | 6,100 | 5,300 to 7,000 | 12 | −42 |
| Catabond 200CZ | 11% HCl acid (27.8%). | *M* | 1.8 | 11,700 | 8,800 to 17,400 | 12 | 13,100 | 10,800 to 16,900 | 12 | +12 | 9,800 | 7,000 to 12,600 | 12 | −16 | 6,600 | 5,700 to 9,500 | 12 | −44 |
| Bakelite XC-3931 | 3% XK-2997 | *M* | 2.7 | 17,300 | 15,200 to 19,900 | 12 | 16,200 | 10,600 to 20,000 | 12 | −6 | 11,600 | 8,800 to 13,600 | 12 | −33 | 9,800 | 4,900 to 11,500 | 12 | −43 |
| Bakelite XC-11749 | 45% XK-11753 | *R* | 3.1 | 18,400 | 15,400 to 19,700 | 12 | 17,700 | 12,500 to 23,100 | 12 | −4 | 12,900 | 8,700 to 15,300 | 12 | −30 | 9,800 | 6,000 to 11,400 | 12 | −47 |
| Catabond 590 | None | *H* | 3.6 | 24,000 | 21,300 to 25,800 | 15 | 26,700 | 23,400 to 29,700 | 15 | +11 | 21,700 | 18,100 to 25,200 | 15 | −10 | 17,000 | 14,800 to 19,000 | 10 | −29 |
| Bakelite XC-3931 | do | *H* | 4.5 | 23,000 | 18,100 to 30,000 | 15 | 25,100 | 22,900 to 28,900 | 15 | +7 | 24,800 | 23,300 to 26,300 | 15 | +5 | 10,700 | 9,100 to 12,800 | 15 | −55 |
| Bakelite XC-11749 | do | *H* | 3.9 | 24,600 | 22,100 to 26,800 | 15 | 27,900 | 23,300 to 29,700 | 15 | +13 | 21,900 | 18,300 to 24,100 | 15 | −11 | 14,200 | 11,500 to 16,000 | 15 | −43 |
| Catabond 200CZ | do | *H* | 4.6 | 24,000 | 21,300 to 25,800 | 15 | 26,500 | 23,000 to 29,200 | 15 | +10 | 25,000 | 19,900 to 27,300 | 15 | +4 | 17,400 | 15,300 to 18,600 | 10 | −28 |
| Cascophen LT-67 | 8% M-18 | *M* | 6.4 | 21,900 | 17,600 to 24,200 | 12 | 25,400 | 23,200 to 27,100 | 12 | +16 | 21,900 | 19,100 to 24,100 | 12 | 0 | 13,900 | 10,400 to 16,200 | 12 | −37 |
| Durez 12041 | None | *H* | 5.0 | 24,700 | 22,400 to 28,700 | 15 | 26,500 | 21,700 to 30,700 | 15 | +8 | 23,800 | 21,300 to 27,100 | 15 | −4 | 17,800 | 15,300 to 21,000 | 15 | −28 |
| Bakelite BC-17540 | 15% BC-17545 | *M* | 7.3 | 20,200 | 17,900 to 21,600 | 30 | ------ | ------ | ------ | ------ | 20,000 | 18,600 to 21,400 | 30 | −1 | 12,800 | 10,800 to 14,200 | 30 | −37 |
| Tego film | None | *H* | 8.2 | 19,700 | 14,400 to 21,000 | 10 | 17,900 | 16,000 to 19,200 | 4 | −9 | 17,500 | 13,900 to 21,700 | 8 | −11 | 19,000[a] | 14,300 to 20,700 | 12 | −4 |
| Amberlite PR-14 | Incorporated with resin. | *H* | 8.4 | 21,800 | 16,000 to 25,300 | 15 | 22,600 | 20,100 to 25,600 | 15 | +4 | 20,500 | 18,600 to 24,400 | 15 | −6 | 13,400 | 8,300 to 16,400 | 15 | −38 |

See footnotes at end of table.

TABLE 4.—*Effect of catalyst and* pH *on flexural strength of resin-bonded birch plywood*—Continued

| Commercial designation of resin | Catalyst added to resin | Classification | pH of unaged panel | Unaged panel | | | Flexural strength data | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Oven-aged panel | | | | Oven-fog-aged panel | | | | Roof-aged panel | | | |
| | | | | Flexural strength | | No. of specimens | Flexural strength | | No. of specimens | Change in strength | Flexural strength | | No. of specimens | Change in strength | Flexural strength | | No. of specimens | Change in strength |
| | | | | Average | Range | | Average | Range | | | Average | Range | | | Average | Range | | |
| **RESORCINOL-FORMALDEHYDE RESINS** | | | | | | | | | | | | | | | | | | |
| | | | | *lb/in.²* | *lb/in.²* | | *lb/in.²* | *lb/in.²* | | *Percent* | *lb/in.²* | *lb/in.²* | | *Percent* | *lb/in.²* | *lb/in.²* | | *Percent* |
| Durez 12490 | 11% formaldehyde. | *R* | 4.8 | 17,500 | 15,400 to 19,100 | 12 | 19,600 | 17,600 to 21,000 | 12 | +12 | 17,500 | 16,500 to 18,900 | 12 | 0 | 10,700 | 9,300 to 12,200 | 12 | −39 |
| Penacolite G-1131 | 20% G-1131B | *R* | 5.1 | 19,200 | 17,100 to 21,800 | 36 | | | | | 21,600 | 19,200 to 25,100 | 36 | +13 | 12,000 | 9,600 to 14,900 | 36 | −38 |
| Bakelite XC-17612 | 20% XK-17618 | *M* | 4.8 | 21,200 | 18,200 to 22,400 | 30 | | | | | 19,800 | 16,300 to 21,900 | 30 | −7 | 12,800 | 10,700 to 14,300 | 28 | −40 |
| Amberlite PR-75B | 22% P-79 | *M* | 5.4 | 20,200 | 17,600 to 22,400 | 36 | | | | | 19,600 | 16,200 to 21,600 | 35 | −3 | 11,000 | 9,200 to 12,700 | 32 | −46 |
| Penacolite G-1124 | 25% G-1124B | *R* | 5.1 | 21,600 | 19,700 to 23,400 | 12 | 23,100 | 21,400 to 24,400 | 12 | +7 | 18,000 | 16,100 to 19,400 | 11 | −17 | 10,100 | 8,200 to 11,800 | 12 | −53 |
| Durite S-3026 | 16% 3026A | *R* | 6.3 | 17,600 | 14,700 to 20,000 | 30 | | | | | 17,500 | 16,200 to 19,200 | 30 | −0.6 | 10,700 | 9,800 to 11,900 | 30 | −39 |
| **PHENOL-RESORCINOL-FORMALDEHYDE RESIN** | | | | | | | | | | | | | | | | | | |
| Durez 12533 | 100% 12534B | *M* | 5.1 | 22,300 | 21,100 to 23,800 | 12 | 23,400 | 21,400 to 26,000 | 12 | +5 | 21,300 | 20,000 to 23,000 | 12 | −5 | 10,700 | 9,400 to 12,800 | 12 | −52 |
| **FURANE RESIN** | | | | | | | | | | | | | | | | | | |
| Resin X | 5% Z-1A | *R* | 2.2 | 17,100 | 14,800 to 20,000 | 36 | | | | | 16,400 | 12,700 to 20,800 | 36 | −5 | 8,500 | 7,000 to 10,800 | 36 | −50 |
| **CASEIN GLUE** | | | | | | | | | | | | | | | | | | |
| Aircraft joint P glue | None | *R* | 8.4 | 18,100 | 14,400 to 20,100 | 12 | 20,700 | 12,300 to 23,600 | 12 | +14 | 17,200 | 12,700 to 18,600 | 12 | −5 | [a] | | | |
| **UNSATURATED POLYESTER RESINS** | | | | | | | | | | | | | | | | | | |
| Laminac | 1% benzoyl peroxide. | *H* | 3.7 | 15,300 | 12,700 to 18,500 | 13 | 19,800 | 12,400 to 23,300 | 15 | +29 | 17,800 | 16,900 to 19,600 | 12 | +16 | 9,000 | 9,400 to 10,800 | 10 | −35 |
| Do | 1% lauroyl peroxide. | *H* | 4.0 | 18,800 | 17,000 to 21,000 | 15 | 19,500 | 15,000 to 20,700 | 15 | +4 | 16,300 | 12,200 to 19,800 | 15 | −13 | 9,500 | 9,000 to 10,600 | 15 | −49 |
| MR-17-A2 | 3% benzoyl peroxide. | *H* | 3.7 | 24,300 | 22,800 to 26,700 | 15 | 23,200 | 20,800 to 25,800 | 15 | −5 | 20,900 | 17,900 to 23,700 | 14 | −14 | 10,100 | 8,600 to 11,800 | 15 | −59 |
| BR-17-B1 | do | *H* | 3.2 | 22,900 | 20,500 to 26,100 | 15 | 22,400 | 19,700 to 27,000 | 15 | −2 | 20,300 | 18,700 to 23,200 | 15 | −11 | 9,700 | 8,900 to 11,300 | 15 | −58 |
| Plaskon 900 | 2% benzoyl peroxide. | *M* | 3.8 | 15,500 | 9,300 to 19,600 | 30 | | | | | 15,500 | 11,200 to 18,800 | 30 | 0 | 7,200 | 6,100 to 10,000 | 17[b] | −54 |
| CR-39 | 5% benzoyl peroxide. | *H* | 3.9 | 24,600 | 21,500 to 27,100 | 20 | 23,800 | 20,900 to 26,700 | 15 | −4 | 24,700 | 21,200 to 27,700 | 15 | +0.4 | 12,300 | 10,800 to 14,000 | 15 | −50 |

[a] Panels delaminated during exposure on roof.
[b] The 3 panels exposed delaminated partially so that only 17 specimens were obtained instead of 20 as planned.

TABLE 5.—*Effect of catalyst and pH on the impact strength of resin-bonded birch plywood*

| Commercial designation of resin | Catalyst added to resin | Classification | pH of unaged panel | Impact strength (edgewise) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Unaged panel | | Oven-aged panel | | | Oven-fog-aged panel | | | Roof-aged panel | | | |
| | | | | Average | Range | Average | Range | No. of specimens | Change in strength | Average | Range | No. of specimens | Change in strength | Average | Range | No. of specimens | Change in strength |
| **RESORCINOL-FORMALDEHYDE RESINS** | | | | | | | | | | | | | | | | | |
| | | | | *lb/in.²* | *lb/in.²* | *lb/in.²* | *lb/in.²* | | *Percent* | *lb/in.²* | *lb/in.²* | | *Percent* | *lb/in.²* | *lb/in.²* | | *Percent* |
| Durez 12490 | 11% formaldehyde | *R* | 4.8 | 2.0 | 1.6 to 2.4 | 2.0 | 1.6 to 2.4 | 12 | 0 | 2.0 | 1.6 to 2.4 | 12 | 0 | 1.6 | 1.2 to 2.0 | 12 | −20 |
| Penacolite G-1131 | 20% G-1131B | *R* | 5.1 | 2.0 | 1.6 to 2.4 | | | | | 2.0 | 1.6 to 2.4 | 36 | 0 | 1.6 | 1.2 to 2.0 | 36 | −20 |
| Bakelite XC-17612 | 20% XK-17618 | *M* | 4.8 | 2.0 | 1.6 to 2.4 | | | | | 2.0 | 1.6 to 2.4 | 30 | 0 | 1.6 | 1.2 to 2.0 | 28 | −20 |
| Amberlite PR-75B | 22% P-79 | *M* | 5.4 | 2.0 | 1.6 to 2.4 | | | | | 2.0 | 1.6 to 2.4 | 35 | 0 | 1.6 | 1.2 to 2.0 | 32 | −20 |
| Penacolite G-1124 | 25% G-1124B | *R* | 5.1 | 2.0 | 1.6 to 2.4 | 2.0 | 1.6 to 2.4 | 12 | 0 | 2.0 | 1.6 to 2.4 | 11 | 0 | 1.6 | 1.2 to 2.0 | 12 | −20 |
| Durite S-3026 | 16% 3026A | *R* | 6.3 | 2.0 | 1.6 to 2.4 | | | | | 2.0 | 1.6 to 2.4 | 30 | 0 | 1.6 | 1.2 to 2.0 | 30 | −20 |
| **PHENOL-RESORCINOL-FORMALDEHYDE RESIN** | | | | | | | | | | | | | | | | | |
| Durez 12533 | 100% 12534B | *M* | 5.1 | 2.0 | 1.6 to 2.4 | 2.0 | 1.6 to 2.4 | 12 | 0 | 2.0 | 1.6 to 2.4 | 12 | 0 | 1.6 | 1.2 to 2.0 | 12 | −20 |
| **FURANE RESIN** | | | | | | | | | | | | | | | | | |
| Resin X | 5% Z-1A | *R* | 2.2 | 2.0 | 1.6 to 2.4 | | | | | 2.0 | 1.6 to 2.4 | 36 | 0 | 1.6 | 1.2 to 2.0 | 36 | −20 |
| **CASEIN GLUE** | | | | | | | | | | | | | | | | | |
| Aircraft joint P glue | None | *R* | 8.4 | 2.0 | 1.6 to 2.4 | 2.0 | 1.6 to 2.4 | 12 | 0 | 2.0 | 1.6 to 2.4 | 12 | 0 | [a] | | | |
| **UNSATURATED POLYESTER RESINS** | | | | | | | | | | | | | | | | | |
| Laminac | 1% benzoyl peroxide | *H* | 3.7 | 2.0 | 1.6 to 2.4 | 2.0 | 1.6 to 2.4 | 13 | 0 | 2.0 | 1.6 to 2.4 | 12 | 0 | 1.6 | 1.2 to 2.0 | 10 | −20 |
| Do | 1% lauroyl peroxide | *H* | 4.0 | 2.0 | 1.6 to 2.4 | 2.0 | 1.6 to 2.4 | 15 | 0 | 2.0 | 1.6 to 2.4 | 15 | 0 | 1.6 | 1.2 to 2.0 | 15 | −20 |
| MR-17-A2 | 3% benzoyl peroxide | *H* | 3.7 | 2.0 | 1.6 to 2.4 | 2.0 | 1.6 to 2.4 | 15 | 0 | 2.0 | 1.6 to 2.4 | 14 | 0 | 1.6 | 1.2 to 2.0 | 15 | −20 |
| BR-17-B1 | do | *H* | 3.2 | 2.0 | 1.6 to 2.4 | 2.0 | 1.6 to 2.4 | 15 | 0 | 2.0 | 1.6 to 2.4 | 15 | 0 | 1.6 | 1.2 to 2.0 | 15 | −20 |
| Plaskon 900 | 2% benzoyl peroxide | *M* | 3.8 | 2.0 | 1.6 to 2.4 | | | | | 2.0 | 1.6 to 2.4 | 30 | 0 | 1.6 | 1.2 to 2.0 | 17[b] | −20 |
| CR-39 | 5% benzoyl peroxide | *H* | 3.9 | 2.0 | 1.6 to 2.4 | 2.0 | 1.6 to 2.4 | 15 | 0 | 2.0 | 1.6 to 2.4 | 15 | 0 | 1.6 | 1.2 to 2.0 | 15 | −20 |

[a] Panels delaminated during exposure on roof.
[b] The 3 panels exposed delaminated partially so that only 17 specimens were obtained instead of 20 as planned.

[a] Panels delaminated during exposure on roof.
[b] The 3 panels exposed delaminated partially so that only 17 specimens were obtained instead of 30 as planned.



| Commercial designation of resin | Catalyst added to resin | Classification | pH of unaged panel | Impact strength (edgewise) | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Unaged panel | | | Oven-aged panel | | | | Oven-fog-aged panel | | | | Roof-aged panel | | | | |
| | | | | Impact strength | | No. of specimens | Impact strength | | No. of specimens | Change in strength | Impact strength | | No. of specimens | Change in strength | Impact strength | | No. of specimens | Change in strength | |
| | | | | Average | Range | | Average | Range | | | Average | Range | | | Average | Range | | | |
| **UREA-FORMALDEHYDE RESINS** | | | | | | | | | | | | | | | | | | | |
| | | | | *ft-lb* | *ft-lb* | | *ft-lb* | *ft-lb* | | *Percent* | *ft-lb* | *ft-lb* | | *Percent* | *ft-lb* | *ft-lb* | | *Percent* |
| Uformite 430 | 10% ammonium chloride. | *R* | 1.9 | 2.0 | 1.4 to 2.5 | 12 | 1.4 | 1.2 to 1.6 | 8 | −30 | 1.3 | 0.8 to 1.8 | 6 | −35 | [b]3.0 | 3.0 to 3.1 | 5 | +50 |
| Do | 10% "Z" | *R* | 2.0 | 2.0 | 1.5 to 2.8 | 6 | 1.4 | 0.8 to 1.6 | 6 | −30 | 1.2 | .9 to 1.6 | 6 | −40 | (a) | | | |
| Do | 10% "Y" | *R* | 2.4 | 2.0 | 1.9 to 2.0 | 6 | 1.3 | 1.1 to 1.5 | 6 | −35 | 1.5 | 1.4 to 1.8 | 6 | −25 | (a) | | | |
| Plaskon 201-2 | 2% "A" | *R* | 3.2 | 2.2 | 1.8 to 2.5 | 6 | 1.8 | 1.6 to 2.2 | 6 | −18 | 1.8 | 1.1 to 3.0 | 6 | −18 | 2.0 | 1.8 to 2.4 | 6 | −9 |
| Casco 5 | 5% "AA" | *R* | 3.4 | 2.2 | 2.0 to 2.4 | 6 | 1.4 | 1.1 to 1.6 | 6 | −36 | 1.7 | 1.5 to 1.9 | 6 | −23 | (a) | | | |
| Plaskon 250-2 | Incorporated with resin. | *R* | 3.6 | 2.2 | 1.8 to 2.8 | 6 | 1.6 | 1.4 to 1.8 | 6 | −27 | 1.8 | 1.8 to 2.1 | 6 | −18 | 2.4 | 1.7 to 2.8 | 6 | +9 |
| Plaskon 107 | 7% B-7 | *H* | 3.8 | 2.8 | 2.6 to 3.1 | 18 | 2.8 | 2.7 to 2.9 | 18 | 0 | 2.3 | 2.2 to 2.3 | 18 | −18 | 1.9 | 1.8 to 1.9 | 18 | −32 |
| Uformite 500 | None | *H* | 5.5 | 2.9 | 2.1 to 3.6 | 18 | 2.9 | 2.2 to 4.5 | 18 | 0 | 2.4 | 2.3 to 2.4 | 18 | −17 | 2.4 | 2.3 to 2.4 | 18 | −17 |
| Casco 5 | do | *H* | 5.7 | 3.0 | 3.0 to 3.2 | 15 | 2.8 | 2.7 to 3.0 | 13 | −7 | 2.5 | 2.0 to 2.9 | 14 | −17 | 2.6 | 1.8 to 3.1 | 14 | −13 |
| Uformite 430 | do | *H* | 4.6 | 3.0 | 2.8 to 3.3 | 18 | 2.6 | 2.5 to 2.9 | 18 | −13 | 2.5 | 2.2 to 2.7 | 18 | −17 | 1.9 | 1.8 to 2.0 | 18 | −37 |
| **UREA-RESORCINOL-FORMALDEHYDE RESINS** | | | | | | | | | | | | | | | | | | | |
| Uformite 500 | 20% Q-107; 0.7% Q-87 | *M* | 5.1 | 2.7 | 2.2 to 3.2 | 6 | 2.8 | 2.4 to 3.0 | 6 | +4 | 1.9 | 1.6 to 2.2 | 3 | −30 | 1.9 | 1.6 to 2.2 | 3 | −30 |
| Plaskon 700-2 | 16% Modifier | *M* | 4.0 | 4.6 | 3.6 to 4.2 | 6 | 3.2 | 2.9 to 3.8 | 6 | −20 | 2.5 | 2.1 to 2.7 | 6 | −38 | 2.1 | 2.0 to 2.1 | 6 | −48 |
| **PHENOL-FORMALDEHYDE RESINS** | | | | | | | | | | | | | | | | | | | |
| Durez 12041 | 10% 7422 | *M* | 1.8 | 2.3 | 2.0 to 2.5 | 6 | 2.1 | 1.6 ro 2.7 | 6 | −9 | 1.6 | 1.2 to 1.8 | 5 | −30 | 1.0 | 1.0 to 1.1 | 6 | −57 |
| Durez 11427 | 10% 7422 | *M* | 1.8 | 3.0 | 2.5 to 3.5 | 6 | 2.0 | 1.8 to 2.1 | 6 | −33 | 1.3 | 0.9 to 2.0 | 6 | −57 | 1.2 | 1.1 to 1.4 | 6 | −60 |
| Catabond 590 | 11% HCl acid (27.8%) | *M* | 1.7 | 1.3 | 1.2 to 1.5 | 6 | 0.7 | 0.5 to 0.8 | 6 | −46 | 0.8 | .7 to 0.9 | 6 | −39 | 0.7 | 0.6 to 0.7 | 6 | −46 |
| Catabond 200-CZ | 11% HCl acid (27.8%) | *M* | 1.8 | 1.4 | 1.3 to 1.6 | 6 | 1.2 | .9 to 1.5 | 6 | −14 | 1.1 | .9 to 1.2 | 6 | −21 | .7 | .6 to 0.7 | 5 | −50 |
| Bakelite XC-3931 | 3% XK-2097 | *M* | 2.7 | 2.2 | 2.0 to 2.4 | 6 | 1.4 | 1.3 to 1.6 | 6 | −36 | 1.5 | 1.4 to 1.5 | 6 | −32 | 1.1 | 1.0 to 1.2 | 6 | −50 |
| Bakelite XC-11749 | 45% XK-11753 | *R* | 3.1 | 2.0 | 1.9 to 2.3 | 6 | 2.0 | 1.6 to 2.7 | 6 | 0 | 1.3 | 1.2 to 1.5 | 6 | −35 | 1.2 | 0.8 to 1.9 | 6 | −40 |
| Catabond 590 | None | *H* | 3.6 | 3.4 | 3.2 to 3.6 | 17 | 3.4 | 3.3 to 3.5 | 18 | 0 | 2.9 | 2.8 to 3.1 | 18 | −15 | 1.9 | 1.9 to 2.0 | 12 | −44 |
| Bakelite XC-3931 | do | *H* | 4.5 | 3.2 | 3.1 to 3.3 | 18 | 3.4 | 2.5 to 3.6 | 18 | +6 | 2.8 | 2.7 to 3.0 | 18 | −13 | 1.6 | 1.3 to 3.0 | 18 | −50 |
| Bakelite XC-11749 | do | *H* | 3.9 | 2.6 | 2.4 to 2.9 | 18 | 3.1 | 2.9 to 3.2 | 18 | +19 | 2.5 | 2.1 to 2.9 | 18 | −4 | 1.6 | 1.4 to 1.8 | 18 | −38 |
| Catabond 200-CZ | do | *H* | 4.6 | 3.5 | 3.2 to 3.6 | 18 | 3.8 | 3.7 to 3.9 | 18 | +9 | 3.0 | 3.0 to 3.1 | 18 | −14 | 1.6 | 1.6 to 1.6 | 12 | −54 |
| Cascophen LT-67 | 8% M-18 | *M* | 6.4 | 2.7 | 2.4 to 3.0 | 6 | 2.6 | 1.9 to 3.9 | 6 | −4 | 2.3 | 2.0 to 2.3 | 6 | −15 | 2.1 | 1.5 to 2.8 | 6 | −22 |
| Durez 12041 | None | *H* | 5.0 | 3.3 | 3.1 to 3.4 | 18 | 3.4 | 3.3 to 3.5 | 18 | −3 | 2.7 | 2.3 to 3.4 | 18 | −18 | 2.0 | 1.9 to 2.2 | 16 | −39 |
| Tego film | Incorporated with resin. | *H* | 8.2 | 3.0 | 2.4 to 3.7 | 23 | 2.8 | 2.6 to 3.0 | 8 | −7 | 2.9 | 2.8 to 2.9 | 8 | −3.3 | [b]2.9 | 2.5 to 3.2 | 8 | −3.3 |
| Amberlite PR-14 | do | *H* | 8.4 | 3.0 | 2.7 to 3.4 | 18 | 3.6 | 2.9 to 3.7 | 18 | +20 | 3.0 | 2.9 to 3.2 | 18 | 0 | 2.2 | 2.2 to 2.2 | 18 | −27 |

Footnotes at end of table, p. 296.

TABLE 5.—*Effect of catalyst and pH on the impact strength of resin-bonded birch plywood*—Continued

| Commercial designation of resin | Catalyst added to resin | Classification | pH of unaged panel | Impact strength (edgewise) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Unaged panel | | | Oven-aged panel | | | | Oven-fog-aged panel | | | | Roof-aged panel | | | |
| | | | | Impact strength | | No. of specimens | Impact strength | | No. of specimens | Change in strength | Impact strength | | No. of specimens | Change in strength | Impact strength | | No. of specimens | Change in strength |
| | | | | Average | Range | | Average | Range | | | Average | Range | | | Average | Range | | |
| **RESORCINOL-FORMALDEHYDE RESINS** | | | | | | | | | | | | | | | | | | |
| | | | | *ft-lb* | *ft-lb* | | *ft-lb* | *ft-lb* | | *Percent* | *ft-lb* | *ft-lb* | | *Percent* | *ft-lb* | *ft-lb* | | *Percent* |
| Durez 12490 | 30% formaldehyde (37%). | *R* | 4.8 | 3.3 | 3.0 to 3.4 | 6 | 3.1 | 2.5 to 3.5 | 6 | −6 | 2.9 | 2.7 to 3.0 | 3 | −12 | 2.9 | 2.7 to 3.0 | 3 | −12 |
| Penacolite G-1124 | 25% g-1124B | *R* | 5.1 | 3.1 | 2.9 to 3.4 | 6 | 2.8 | 2.5 to 3.1 | 6 | −10 | 3.3 | 2.3 to 4.5 | 6 | +6 | 1.7 | 1.3 to 2.6 | 6 | −45 |
| **PHENOL-RESORCINOL-FORMALDEHYDE RESIN** | | | | | | | | | | | | | | | | | | |
| Durez 12533 | 100% 12534B | *M* | 5.1 | 3.5 | 3.4 to 3.6 | 6 | 2.3 | 1.9 to 2.8 | 6 | −34 | 2.3 | 2.0 to 2.8 | 6 | −34 | 2.3 | 2.1 to 2.8 | 6 | −34 |
| **CASEIN GLUE** | | | | | | | | | | | | | | | | | | |
| Aircraft joint P glue | None | *R* | 8.4 | 5.0 | 4.2 to 5.1 | 6 | 3.9 | 3.6 to 4.1 | 6 | −22 | 3.2 | 2.3 to 4.0 | 5 | −36 | (a) | | | |
| **UNSATURATED POLYESTER RESINS** | | | | | | | | | | | | | | | | | | |
| Laminac | 1% benzoyl peroxide | *H* | 3.7 | 3.9 | 3.7 to 4.2 | 18 | 4.0 | 3.8 to 4.1 | 18 | +3 | 3.6 | 3.3 to 4.0 | 18 | −8 | 1.9 | 1.9 to 2.0 | 12 | −51 |
| Do | 1% lauroyl peroxide | *H* | 4.0 | 4.7 | 4.4 to 5.1 | 18 | 4.8 | 3.5 to 5.8 | 18 | −2 | 4.2 | 3.6 to 4.7 | 18 | −11 | 2.1 | 1.6 to 2.7 | 18 | −55 |
| MR-17-A2 | 3% benzoyl peroxide | *H* | 3.7 | 3.5 | 3.0 to 4.0 | 18 | 3.3 | 1.5 to 4.4 | 18 | −6 | 3.2 | 3.1 to 3.3 | 18 | −9 | 1.9 | 1.6 to 2.1 | 18 | −46 |
| MR-17-B1 | do | *H* | 3.2 | 4.6 | 4.3 to 4.8 | 18 | 4.0 | 3.4 to 4.6 | 18 | −13 | 4.2 | 3.6 to 5.0 | 18 | −9 | 2.4 | 2.4 to 2.5 | 18 | −48 |
| CR-39 | 5% benzoyl peroxide | *H* | 3.9 | 3.8 | 3.3 to 4.1 | 18 | 4.2 | 3.5 to 4.6 | 24 | +11 | 4.0 | 3.5 to 4.4 | 18 | +5 | 2.9 | 2.5 to 3.7 | 18 | −24 |

(a) Panels delaminated during exposure on roof.
(b) Panels exposed for only 6 months.



| Commercial designation of resin | Catalyst added to resin | Classification | pH of unaged panel | Shear strength data (a) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Unaged panel | | | Oven-aged panel | | | | Oven-fog-aged panel | | | | Roof-aged panel | | | |
| | | | | Shear strength | | No. of specimens | Shear strength | | No. of specimens | Change in strength | Shear strength | | No. of specimens | Change in strength | Shear strength | | No. of specimens | Change in strength |
| | | | | Average | Range | | Average | Range | | | Average | Range | | | Average | Range | | |
| **RESORCINOL-FORMALDEHYDE RESINS** | | | | | | | | | | | | | | | | | | |
| | | | | *lb/in²* | *lb/in²* | | *lb/in²* | *lb/in²* | | *Percent* | *lb/in²* | *lb/in²* | | *Percent* | *lb/in²* | *lb/in²* | | *Percent* |
| Durez 12490 | 30% formaldehyde (37%). | *R* | 4.8 | 2,200 | 2,100 to 2,300 | 6 | 2,200 | 2,100 to 2,300 | 6 | 0 | 2,200 | 2,100 to 2,300 | 3 | 0 | 2,200 | 2,100 to 2,300 | 3 | 0 |
| Penacolite G-1124 | 25% g-1124B | *R* | 5.1 | 2,200 | 2,100 to 2,300 | 6 | 2,200 | 2,100 to 2,300 | 6 | 0 | 2,200 | 2,100 to 2,300 | 6 | 0 | 2,200 | 2,100 to 2,300 | 6 | 0 |
| **PHENOL-RESORCINOL-FORMALDEHYDE RESIN** | | | | | | | | | | | | | | | | | | |
| Durez 12533 | 100% 12534B | *M* | 5.1 | 2,200 | 2,100 to 2,300 | 6 | 2,200 | 2,100 to 2,300 | 6 | 0 | 2,200 | 2,100 to 2,300 | 6 | 0 | 2,200 | 2,100 to 2,300 | 6 | 0 |
| **CASEIN GLUE** | | | | | | | | | | | | | | | | | | |
| Aircraft joint P glue | None | *R* | 8.4 | 2,200 | 2,100 to 2,300 | 6 | 2,200 | 2,100 to 2,300 | 6 | 0 | 2,200 | 2,100 to 2,300 | 5 | 0 | (b) | | | |
| **UNSATURATED POLYESTER RESINS** | | | | | | | | | | | | | | | | | | |
| Laminac | 1% benzoyl peroxide | *H* | 3.7 | 2,200 | 2,100 to 2,300 | 18 | 2,200 | 2,100 to 2,300 | 18 | 0 | 2,200 | 2,100 to 2,300 | 18 | 0 | 2,200 | 2,100 to 2,300 | 12 | 0 |
| Do | 1% lauroyl peroxide | *H* | 4.0 | 2,200 | 2,100 to 2,300 | 18 | 2,200 | 2,100 to 2,300 | 18 | 0 | 2,200 | 2,100 to 2,300 | 18 | 0 | 2,200 | 2,100 to 2,300 | 18 | 0 |
| MR-17-A2 | 3% benzoyl peroxide | *H* | 3.7 | 2,200 | 2,100 to 2,300 | 18 | 2,200 | 2,100 to 2,300 | 18 | 0 | 2,200 | 2,100 to 2,300 | 18 | 0 | 2,200 | 2,100 to 2,300 | 18 | 0 |
| MR-17-B1 | do | *H* | 3.2 | 2,200 | 2,100 to 2,300 | 18 | 2,200 | 2,100 to 2,300 | 18 | 0 | 2,200 | 2,100 to 2,300 | 18 | 0 | 2,200 | 2,100 to 2,300 | 18 | 0 |
| CR-39 | 5% benzoyl peroxide | *H* | 3.9 | 2,200 | 2,100 to 2,300 | 18 | 2,200 | 2,100 to 2,300 | 24 | 0 | 2,200 | 2,100 to 2,300 | 18 | 0 | 2,200 | 2,100 to 2,300 | 18 | 0 |

(a) Panels delaminated during exposure on roof.
(b) Panels exposed for only 6 months.

| Commercial designation of resin | Catalyst added to resin | Classification | pH of unaged panel | Shear strength data [a] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Unaged panel | | | Oven-aged panel | | | | Oven-fog-aged panel | | | | Roof-aged panel | | | |
| | | | | Shear strength | | No. of specimens | Shear strength | | No. of specimens | Change in strength | Shear strength | | No. of specimens | Change in strength | Shear strength | | No. of specimens | Change in strength |
| | | | | Average | Range | | Average | Range | | | Average | Range | | | Average | Range | | |
| **UREA-FORMALDEHYDE RESINS** | | | | | | | | | | | | | | | | | | |
| | | | | *lb/in.²* | *lb/in.²* | | *lb/in.²* | *lb/in.²* | | *Percent* | *lb/in.²* | *lb/in.²* | | *Percent* | *lb/in.²* | *lb/in.²* | | *Percent* |
| Uformite 430 | 10% ammonium chloride. | *R* | 1.9 | 220 | 180 to 260 | 5 | 200 | 180 to 220 | 4 | −9 | 130 | 120 to 130 | 3 | −41 | 200 | 180 to 220 | [2] 2 | −9 |
| Do | 10% "Z" | *R* | 2.0 | 480 | 430 to 500 | 4 | 400 | 390 to 420 | 3 | −17 | 320 | 280 to 360 | 6 | −33 | [b] | | | |
| Do | 10% "Y" | *R* | 2.4 | 580 | 520 to 640 | 5 | 450 | 438 to 470 | 2 | −22 | 420 | 380 to 510 | 5 | −28 | [b] | | | |
| Plaskon 201–2 | 2% "A" | *R* | 3.2 | 620 | 560 to 670 | 3 | 550 | | 1 | −11 | 570 | 450 to 640 | 3 | −8 | 540 | 500 to 640 | 6 | −13 |
| Casco 5 | 5% "AA" | *R* | 3.4 | 600 | 530 to 670 | 4 | 700 | | 1 | +17 | 630 | 560 to 680 | 3 | +5 | [b] | | | |
| Plaskon 250–2 | Incorporated with resin. | *R* | 3.6 | 680 | | 1 | [d] | | | | 590 | | 1 | −13 | 480 | 430 to 520 | 4 | −29 |
| Plaskon 107 | 7% B–7 | *H* | 3.8 | 740 | 680 to 800 | 2 | [d] | | | | 680 | | 1 | −8 | 540 | 450 to 640 | 6 | −27 |
| Uformite 500 | None | *H* | 5.5 | 740 | 680 to 810 | 2 | [d] | | | | 710 | 690 to 720 | 2 | −4 | [d] | | | |
| Casco 5 | do | *H* | 5.7 | [d] | | | [d] | | | | [d] | | | | [d] | | | |
| Uformite 430 | do | *H* | 4.6 | 820 | 720 to 880 | 4 | 790 | | 1 | | [d] | | | −4 | [d] | | | |
| **UREA-RESORCINOL-FORMALDEHYDE RESINS** | | | | | | | | | | | | | | | | | | |
| Uformite 500 | 20% Q–107; 0.7% Q–87 | *M* | 5.1 | 730 | 680 to 810 | 3 | [d] | | | | 650 | | 1 | −11 | 620 | 600 to 630 | 2 | −15 |
| Plaskon 700–2 | 16% modifier | *M* | 4.6 | 810 | 780 to 830 | 3 | 750 | | 1 | −7 | [d] | | | | [d] | | | |
| **PHENOL-FORMALDEHYDE RESINS** | | | | | | | | | | | | | | | | | | |
| Dures 12041 | 10% 7422 | *M* | 1.8 | [d] | | | [d] | | | | [d] | | | | [d] | | | |
| Dures 11427 | 10% 7422 | *M* | 1.8 | [c] | | | [d] | | | | [d] | | | | [d] | | | |
| Catabond 590 | 11% HCl acid (27.8%) | *M* | 1.7 | [d] | | | [d] | | | | [d] | | | | [d] | | | |
| Catabond 200–CZ | 11% HCl acid (27.8%) | *M* | 1.8 | [d] | | | [d] | | | | [d] | | | | [d] | | | |
| Bakelite XC–3031 | 3% XK–2997 | *M* | 2.7 | 640 | | 1 | 580 | 570 to 590 | 2 | −9 | [d] | | | | [d] | | | |
| Bakelite XC–11749 | 45% XK–11753 | *R* | 3.1 | 390 | 370 to 410 | 2 | 570 | | 1 | +46 | 330 | | 1 | −15 | [d] | | | |
| Catabond 590 | None | *H* | 3.6 | 780 | 760 to 810 | 3 | [d] | | | | 790 | | 1 | +1 | [d] | | | |
| Bakelite XC–3031 | do | *H* | 4.5 | [d] | | | 710 | 690 to 740 | 3 | | 710 | 690 to 740 | 3 | | [d] | | | |
| Bakelite XC–11749 | do | *H* | 3.9 | 750 | 700 to 820 | 4 | 700 | 590 to 760 | 4 | −7 | 740 | 670 to 780 | 3 | −1 | [d] | | | |
| Catabond 200 CZ | do | *H* | 4.6 | 770 | 720 to 810 | 2 | [d] | | | | [d] | | | | [d] | | | |
| Cascophen LT–67 | 8% M–18 | *M* | 6.4 | 640 | 580 to 690 | 6 | 670 | 650 to 710 | 3 | +5 | 780 | 770 to 800 | 2 | +22 | [d] | | | |
| Durez 12041 | None | *H* | 5.0 | 750 | 680 to 830 | 4 | 840 | 790 to 890 | 2 | +12 | 760 | 720 to 800 | 2 | +1 | [d] | | | |
| Tego Film | Incorporated with resin. | *H* | 8.2 | 600 | 390 to 1,200 | 8 | 450 | 420 to 520 | 4 | −25 | 780 | 620 to 1,030 | 4 | +30 | 470 | 400 to 520 | [2] 4 | −22 |
| Amberlite PR–14 | do | *H* | 8.4 | 770 | 660 to 930 | 5 | [d] | | | | 730 | 440 to 1,020 | 5 | −5 | 600 | 380 to 780 | 3 | −22 |

Footnotes at end of table, p. 298.

TABLE 6.—*Effect of catalyst and* pH *on the shear strength of resin-bonded birch plywood*—Continued

| Commercial designation of resin | Catalyst added to resin | Classification | pH of unaged panel | Shear strength data [a] | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Unaged panel | | | Oven-aged panel | | | | Oven-fog-aged panel | | | | Roof-aged panel | | | |
| | | | | Shear strength | | No. of specimens | Shear strength | | No. of specimens | Change in strength | Shear strength | | No. of specimens | Change in strength | Shear strength | | No. of specimens | Change in strength |
| | | | | Average | Range | | Average | Range | | | Average | Range | | | Average | Range | | |
| **RESORCINOL-FORMALDEHYDE RESINS** | | | | | | | | | | | | | | | | | | |
| | | | | *lb/in.²* | *lb/in.²* | | *lb/in.²* | *lb/in.²* | | *Percent* | *lb/in.²* | *lb/in.²* | | *Percent* | *lb/in.²* | *lb/in.²* | | *Percent* |
| Durez 12490 | 30% formaldehyde (37%). | *R* | 4.8 | 780 | 610 to 900 | 6 | 740 | 720 to 800 | 4 | −5 | 610 | 530 to 680 | 5 | −22 | 670 | 600 to 700 | 3 | −14 |
| Penacolite G–1124 | 25% G–1124B | *R* | 5.1 | 870 | 860 to 870 | 3 | 820 | 740 to 900 | 2 | −6 | 900 | ..... | 1 | +3 | (c) | ..... | ..... | ..... |
| **PHENOL-RESORCINOL-FORMALDEHYDE RESIN** | | | | | | | | | | | | | | | | | | |
| Durez 12533 | 100% 12534B | *M* | 5.1 | 750 | 710 to 810 | 6 | 780 | ..... | 1 | +4 | 700 | 670 to 700 | 3 | −7 | (c) | ..... | ..... | ..... |
| **CASEIN GLUE** | | | | | | | | | | | | | | | | | | |
| Aircraft joint P glue | None | *R* | 8.4 | 850 | 690 to 1,040 | 6 | 860 | ..... | 1 | +1 | 560 | 420 to 640 | 6 | −34 | (b) | ..... | ..... | ..... |
| **UNSATURATED POLYESTER RESINS** | | | | | | | | | | | | | | | | | | |
| Laminac | 1% benzoyl peroxide | *H* | 3.7 | 520 | 280 to 640 | 6 | 540 | 490 to 600 | 6 | +4 | 460 | 390 to 520 | 6 | −12 | 500 | 470 to 540 | 4 | −4 |
| Do | 1% lauroyl peroxide | *H* | 4.0 | 500 | 470 to 550 | 6 | 450 | 380 to 500 | 6 | −10 | 440 | 320 to 490 | 6 | −12 | 420 | 390 to 440 | 6 | −16 |
| MR–17–A2 | 3% benzoyl peroxide | *H* | 3.7 | 650 | 590 to 750 | 6 | 700 | 680 to 720 | 4 | +8 | 650 | 600 to 740 | 5 | 0 | (c) | ..... | ..... | ..... |
| MR–17–B1 | do | *H* | 3.2 | 700 | 670 to 770 | 6 | 700 | 670 to 750 | 4 | 0 | 730 | 690 to 780 | 5 | +4 | (c) | ..... | ..... | ..... |
| CR–39 | 5% benzoyl peroxide | *H* | 3.9 | 870 | 660 to 960 | 6 | 830 | 710 to 900 | 3 | −5 | 920 | 870 to 930 | 3 | +6 | (c) | ..... | ..... | ..... |

[a] Six specimens were tested in each case; those which broke in tension were not included in computing the shear strength.
[b] Panels delaminated during exposure on roof.
[c] Panels exposed for only 6 months.
[d] All specimens broke in tension rather than shear.

TABLE 7.—*Effect of catalysts and* pH *on the delamination of resin-bonded birch plywood*

| Commercial designation of resin | Catalyst added to resin | Classification | pH of unaged panel | Condition of specimen after delamination test * | | | |
|---|---|---|---|---|---|---|---|
| | | | | Unaged panel | Over-aged panel | Oven-fog-aged panel | Roof-aged panel |
| **UREA-FORMALDEHYDE RESINS** | | | | | | | |
| mite 430 | 10% ammonium chloride | *R* | 1.9 | | | | |
| Do | 10% "Z" | *R* | 2.0 | D (1) | D (2) | D (1) | DR |
| Do | 10% "Y" | *R* | 2.4 | D (1) | D (2) | D (2) | DR |
| kon 201-2 | 2% "A" | *R* | 3.2 | D (3) | D (4) | D (3) | D (1) |
| re 5 | 5% "AA" | *R* | 3.4 | D (2) | D (2) | D (2) | DR |
| kon 250-2 | Incorporated with resin | *R* | 3.6 | D (2) | D (4) | D (2) | D (1) |
| kon 107 | 7% B-7 | *H* | 3.8 | D (3) | D (4) | D (3) | D (1) |
| mite 500 | None | *H* | 5.5 | ND; F (5) | ND; F (5) | ND; F (5) | D (5) |
| re 5 | do | *H* | 5.7 | SD (1); F (5) | D (1) | D (1) | D (1) |
| mite 430 | do | *H* | 4.6 | SD (1); F (5) | SD (1); F (5) | SD (1); F (5) | D (5) |
| **UREA-RESORCINOL-FORMALDEHYDE RESINS** | | | | | | | |
| mite 900 | 20% Q-107; 0.7% Q-87 | *M* | 5.1 | ND; F (5) | ND; F (5) | ND; F (5) | D (5) |
| kon 700-2 | 16% modifier | *M* | 4.6 | ND; F (5) | ND; F (5) | ND; F (5) | D (5) |
| **PHENOL-FORMALDEHYDE RESINS** | | | | | | | |
| ex 12041 | 10% 7422 | *M* | 1.8 | ND; B (5) | ND; B (5) | ND; B (5) | ND; B (5) |
| ex 11427 | 10% 7422 | *M* | 1.8 | ND; B (5) | ND; B (5) | ND; B (5) | ND; B (5) |
| abond 890 | 11% hydrochloric acid (27.8%) | *M* | 1.7 | ND; B (5) | ND; B (5) | ND; B (5) | ND; B (5) |
| abond 200-CZ | do | *M* | 1.8 | ND; B (5) | ND; B (5) | ND; B (5) | ND; B (5) |
| elite XC-3931 | 3% XK-2997 | *M* | 2.7 | ND; B (5) | ND; B (5) | ND; B (5) | ND; B (5) |
| elite XC-11749 | 45% XK-11783 | *R* | 3.1 | ND; B (5) | ND; B (5) | ND; B (5) | ND; B (5) |
| abond 890 | None | *H* | 3.6 | ND; F (5) | ND; F (5) | ND; F (5) | ND; B (5) |
| elite XC-3931 | do | *H* | 4.5 | ND; F (5) | ND; F (5) | ND; F (5) | ND; B (5) |
| elite XC-11749 | do | *H* | 3.9 | ND; F (5) | ND; F (5) | ND; F (5) | ND; B (5) |
| abond 200-CZ | do | *H* | 4.6 | ND; F (5) | ND; F (5) | ND; F (5) | ND; B (5) |
| ophen LT-67 | 8% M-18 | *M* | 6.4 | ND; F (5) | ND; F (5) | ND; B (5) | ND; B (5) |
| ex 12041 | None | *H* | 5.0 | ND; F (5) | ND; F (5) | ND; F (5) | ND; B (5) |
| e Film | Incorporated with resin | *H* | 8.2 | | | | |
| berlite PR-14 | do | *H* | 8.4 | ND; F (5) | ND; F (5) | ND; F (5) | ND; B (5) |
| **RESORCINOL-FORMALDEHYDE RESINS** | | | | | | | |
| ex 12400 | 30% formaldehyde (37%) | *R* | 4.8 | ND; F (5) | ND; F (5) | ND; F (5) | ND; B (5) |
| acolite G-1124 | 25% G-1124 B | *R* | 5.1 | ND; F (5); W | ND; F (5); W | ND; F (5); W | ND; B (5); W |
| **PHENOL-RESORCINOL-FORMALDEHYDE RESIN** | | | | | | | |
| ex 12533 | 100% 12534 B | *M* | 5.1 | ND; F (5) | ND; F (5) | ND; F (5) | ND; B (5) |
| **CASEIN GLUE** | | | | | | | |
| raft Joint P Glue | None | *R* | 8.4 | ND; F (5); W | ND; F (5); W | ND; F (5); W | DR |
| **UNSATURATED POLYESTER RESINS** | | | | | | | |
| minse | 1% benzoyl peroxide | *H* | 3.7 | SD (1); F (5) | SD (1); F (5) | SD (1); F (5) | SD (5); F (5) |
| Do | 1% lauroyl peroxide | *H* | 4.0 | SD (1); F (5) | SD (1); F (5) | SD (1); F (5) | SD (5); F (5) |
| R-17-A2 | 3% benzoyl peroxide | *H* | 3.7 | ND; F (5) | ND; F (5) | ND; F (5) | SD (5); F (5) |
| R-17-B1 | do | *H* | 3.2 | ND; F (5) | ND; F (5) | ND; F (5) | SD (5); F (5) |
| R-19 | 5% benzoyl peroxide | *H* | 3.9 | ND; F (5) | ND; F (5) | ND; F (5) | SD (5); F (5) |

* The specimens were subjected to 5 cycles of immersion in boiling water and drying, described on page 286. Figure in parentheses refers to cycle in which servation was made. Abbreviations are as follows:

*D*=delaminated.
*SD*=slightly delaminated.
*ND*=no delamination.
*DR*=delaminated during exposure treatment on roof.
*W*=warped.
*B*=brittle.
*F*=flexible.

The failure of the urea-formaldehyde resin-bonded materials in the delamination test is also affected by the pH of the plywood. The critical value in this test appears to be between 3.8 and 4.6 for both the unaged and the aged specimens.

Three of the panels with a low pH delaminated during exposure. This indicates that the loss in strength on roof aging can be attributed to both deterioration of the wood and deterioration of the resin.

### (b) Phenolic Resins

An examination of the values in table 8 for the flexural, impact, and shear strengths of the phenolic resin-bonded panels shows that the presence of acid catalyst causes a decrease in these properties in the unaged panels in every case. This decrease was noticed especially with the panels prepared with the Catabond resins 590 and 200CZ, wherein concentrated hydrochloric acid catalysts were used. It is well known that hydrochloric acid has a decidedly deleterious effect on most woods.

No failure of the phenolic resin-bonded composites occurred in the delamination test. The unaged and laboratory aged specimens with pH values of 3.1 or less were brittle in the flexibility test on the 4-in. mandrel. With exception, those with pH values of 3.6 or were flexible throughout this test.

### (c) Other Resins

The remaining adhesives tested, which incl resorcinol, furane, casein, and unsaturated poly types, produced panels of pH 3.2 or greater, the exception of the furane resin panel which a pH of 2.2. These adhesives did not und marked deterioration in strength when subje to the laboratory aging tests. The pronou reduction in strength which occurred under aging conditions is attributable mainly to deter tion of the uncoated wood. However, strengths of the roof-aged panels made with t resins were markedly inferior to those of the aged panel made with the best phenol-formaldeh resins. It is significant that in the roof-a tests conducted as part of this investigation, in the case of the casein and some urea- maldehyde glues had the breakdown at the b progressed sufficiently to make strength tes the roof-aged panels impossible.

TABLE 8.—*Effect of catalyst and* pH *on flexural, impact, and shear strengths of resin-bonded birch plywood*

| Commercial designation of resin | Catalyst added to resin | pH of unaged panel | Decrease in flexural strength [a] | | | | Decrease in Izod impact strength [a] | | | | Decrease in shear strength | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Unaged panel | Oven-aged panel | Oven-fog-aged panel | Roof-aged panel | Unaged panel | Oven-aged panel | Oven-fog-aged panel | Roof-aged panel | Unaged panel | Oven-aged panel | Oven-fog-aged panel | R |
| **UREA-FORMALDEHYDE RESINS** | | | | | | | | | | | | | | |
| | | | *Per-cent* | *Per-cent* | *Per-cent* | *Per-cent* | *Per-cent* | *Per-cent* | *Per-cent* | *Per-cent* | *Per-cent* | *Per-cent* | *Per-cent* | |
| Uformite 430 | None | 4.6 | | | | | | | | | | | | |
| | 10% "Y" | 2.4 | 30 | 39 | 34 | (b) | 33 | 50 | 40 | (b) | 29 | 43 | (c) | |
| | 10% "Z" | 2.0 | 37 | 45 | 47 | (b) | 33 | 46 | 52 | (b) | 41 | 49 | (c) | |
| | 10% NHCl | 1.9 | 42 | 51 | 61 | (b) | 33 | 46 | 48 | (b) | 73 | 75 | (c) | |
| Casco 5 | None | 5.7 | | | | | | | | | | | | |
| | 5% "AA" | 3.4 | 11 | 27 | 26 | (b) | 27 | 50 | 32 | (b) | (c) | (c) | (c) | |
| **PHENOLIC RESINS** | | | | | | | | | | | | | | |
| Catabond 590 | None | 3.6 | | | | | | | | | | | | |
| | 11% HCl acid (27.8%) | 1.7 | 56 | 58 | 57 | 64 | 62 | 79 | 72 | 63 | (c) | (c) | (c) | |
| Catabond 200-CZ | None | 4.6 | | | | | | | | | | | | |
| | 11% HCl acid (27.8%) | 1.8 | 51 | 51 | 61 | 62 | 60 | 68 | 63 | 56 | (c) | (c) | (c) | |
| Bakelite XC-11749 | None | 3.9 | | | | | | | | | | | | |
| | 45% XK-11753 | 3.1 | 25 | 37 | 41 | 31 | 23 | 36 | 48 | 25 | 48 | 19 | 55 | |
| Bakelite XC-3931 | None | 4.5 | | | | | | | | | | | | |
| | 3% XK-2997 | 2.7 | 27 | 35 | 53 | 8 | 31 | 50 | 46 | 31 | (c) | 18 | (c) | |
| Durez 12041 | None | 5.0 | | | | | | | | | | | | |
| | 10% 7422 | 1.8 | 21 | 28 | 43 | 46 | 30 | 38 | 41 | 50 | (c) | (c) | (c) | |

[a] Decrease in strength for the unaged, oven-aged, oven-fog-aged, and roof-aged panels, respectively, is calculated on the basis of the strength of the un oven-aged, oven-fog-aged, and roof-aged panels, respectively, made without catalyst.

[b] Panels delaminated during exposure on roof.

[c] Panels containing catalyst or reference uncatalyzed panels failed in tension rather than shear.

## Effect of Acidic and Basic Catalysts on Strength of Plywood

The outstanding feature of the experiments in ch various acids and alkalies were added to resorcinol-formaldehyde and phenol-formalde- e resins (figs. 1, 2, 3, and 4) was their apparent orption by the resin. Although relatively e amounts of the catalysts were added to duce resin solutions of low pH, the resin films plywood panels had pH values considerably her than those of their respective solutions. The titration curves show that there is a definite mical neutralization reaction between the nolic type resins and acid and alkali, respec- ly. The amount of acid or acid-generating alysts added to cure this type of resinous adhesive at room temperatures is generally greater than the neutral equivalent of the resin. As this additional acid is not destroyed or is only loosely bound to the resin, it is free to cause deterioration of the materials in the structure.

The flexural strengths of the unaged panels made with the resorcinol-formaldehyde resin (table 9) did not undergo a significant decrease with increasing acidity of the resin solution. However, the oven-fog aging conditions brought about a substantial reduction in strength which correlated with decrease in pH. Thus, although the pH of the unaged panels in many instances appeared to be beyond the critical acid range, the acid that had been absorbed by the resin was available to bring about deterioration of the panel under the aging conditions (fig. 8). The strong acids, such

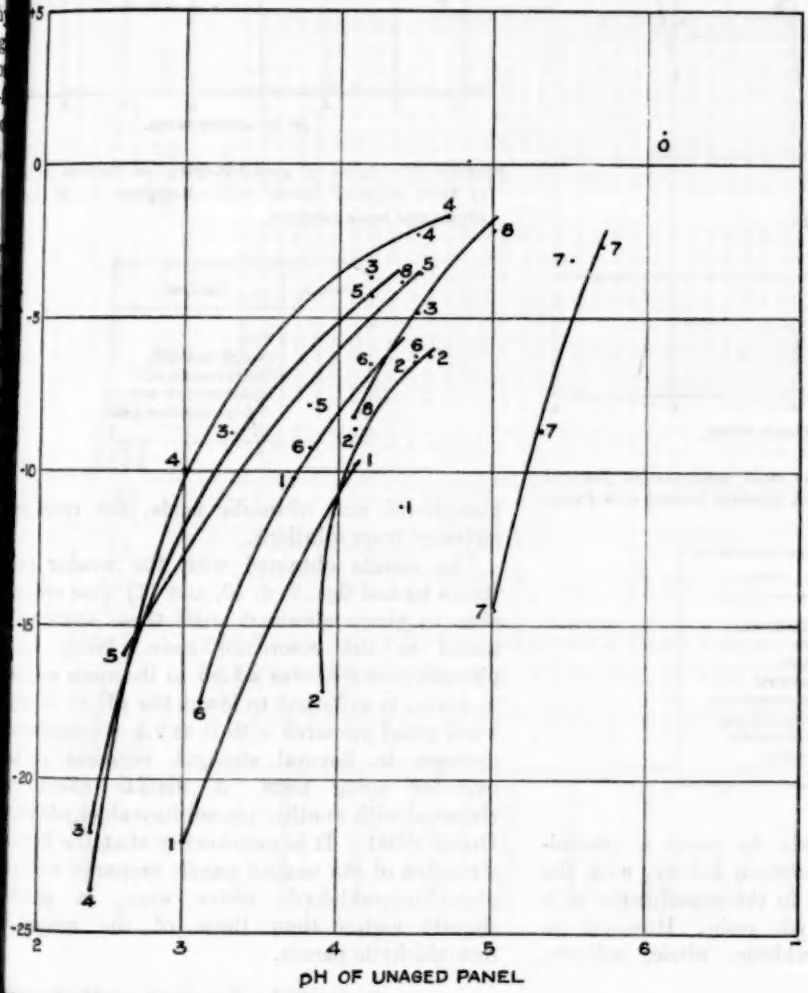



FIGURE 8.—*Effect of oven-fog-aging on flexural strength of birch plywood bonded with Penacolite G–1131, using various acid catalysts.*

| Sample | Acid |
|---|---|
| 0 | None |
| 1 | Hydrochloric |
| 2 | Nitric |
| 3 | Sulfuric |
| 4 | Phosphoric |
| 5 | Hypophosphorous |
| 6 | Benzenesulfonic |
| 7 | Trichloroacetic |
| 8 | Nitranilic |

as hydrochloric, nitric, and sulfuric acids, had only slightly more deteriorating action than the weaker types, such as nitranilic and hypophosphorous acids (fig. 9).

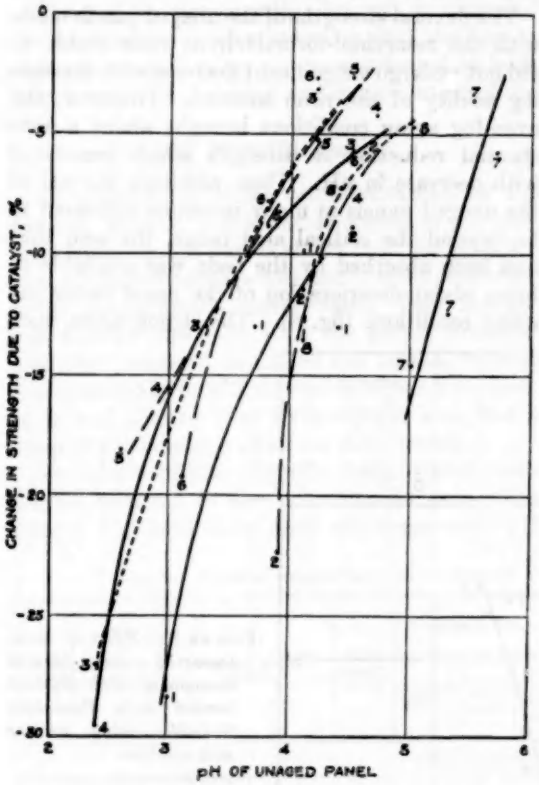



FIGURE 9.—*Effect of various acid catalysts on flexural strength of oven-fog-aged birch plywood bonded with Penacolite G–1131.*

| Sample | Acid |
|---|---|
| 1 | Hydrochloric |
| 2 | Nitric |
| 3 | Sulfuric |
| 4 | Phosphoric |
| 5 | Hypophosphorous |
| 6 | Benzenesulfonic |
| 7 | Trichloroacetic |
| 8 | Nitranilic |

An attempt was made to treat a phenol-formaldehyde resin, Cascophen LT–67, with the same series of acids used in the experiments with the resorcinol-formaldehyde resin. However, in the presence of hydrochloric, nitric, sulfuric, phosphoric, and nitranilic acids, the resin pr cipitated from solutions.

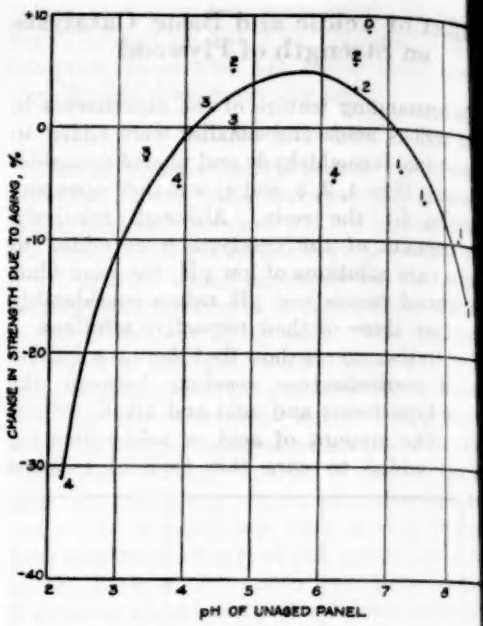



FIGURE 10.—*Effect of oven-fog-aging on flexural stren of birch plywood bonded with Cascophen LT–67, wi acidic and basic catalysts.*

| Sample | Catalyst |
|---|---|
| 0 | None |
| 1 | Sodium hydroxide |
| 2 | Trichloroacetic acid |
| 3 | Benzenesulfonic acid |
| 4 | Hypophosphorous acid |

The results obtained with the weaker aci (table 10 and figs. 3, 4, 10, and 11) were compa able to those obtained with these same aci added to the resorcinol resin. When hyp phosphorous acid was added to the resin soluti in amounts sufficient to lower the pH of the p wood panel prepared with it to 2.2, a considerab decrease in flexural strength occurred in th oven-fog aging tests. A similar effect w observed with another phenol-formaldehyde resi Durez 12041. It is noteworthy that the flexur strengths of the unaged panels prepared with th phenol-formaldehyde resins were, in genera slightly higher than those of the resorcino formaldehyde panels.

| Catalyst added to resin | Milliequivalents of catalyst per 100 g of resin | Density of panel | Resin content of panel | pH | | | | | Flexural strength data | | | | | | | | | | Change in strength due to catalyst [b] | | | Change in strength due to aging [c] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Unaged panel | | | Oven-fog-aged panel | | | Roof-aged panels | | | | | | | | |
| | | | | Resin solution | Resin film | Unaged panel | Oven-fog-aged panel | Roof-aged panel | Flexural strength | | No. of specimens | Flexural strength | | No. of specimens | Flexural strength | | No. of specimens | Unaged panel | Oven-fog-aged panel | Roof-aged panel | Oven-fog-aged panel | Roof-aged panel |
| | | | | | | | | | Average | Range | | Average | Range | | Average | Range | | | | | | |
| | | g/cm³ | Percent | | | | | | lb/in² | lb/in² | | lb/in² | lb/in² | | lb/in² | lb/in² | | Percent | Percent | Percent | Percent | Percent |
| None | | 0.93 | 27.1 | 7.3 | 6.5 | 6.1 | 5.5 | 3.7 | 19,100 | 17,600 to 20,600 | 36 | 19,300 | 17,900 to 20,500 | 36 | 11,100 | 10,200 to 12,000 | 36 | ------ | ------ | ------ | +1.0 | −41.9 |
| Hydrochloric acid | 19 | .90 | 22.4 | 4.1 | 4.1 | 4.4 | 3.9 | 3.4 | 18,900 | 16,900 to 20,600 | 36 | 16,800 | 15,600 to 17,700 | 36 | 10,300 | 9,400 to 11,800 | 36 | −1.0 | −13.0 | −7.2 | −11.1 | −45.5 |
| | 24 | .91 | 24.0 | 1.5 | 2.5 | 4.1 | 3.8 | 3.5 | 19,300 | 17,200 to 20,400 | 36 | 17,400 | 15,000 to 18,800 | 36 | 10,300 | 9,000 to 11,500 | 36 | +1.0 | −9.8 | −7.2 | −9.8 | −46.6 |
| | 32 | .89 | 22.4 | 0.5 | 1.8 | 3.7 | 3.4 | 3.4 | 18,700 | 17,300 to 19,700 | 36 | 16,800 | 15,100 to 18,700 | 36 | 9,900 | 6,700 to 11,200 | 36 | −2.1 | −13.0 | −10.8 | −10.2 | −47.1 |
| | 64 | .91 | 23.5 | .6 | 1.3 | 3.0 | 3.2 | 3.2 | 17,700 | 15,000 to 20,500 | 36 | 13,800 | 10,100 to 16,200 | 36 | 8,200 | 4,100 to 11,000 | 60 | −7.3 | −28.5 | −26.6 | −22.0 | −51.7 |
| Nitric acid | 19 | .88 | 21.9 | 5.3 | 4.4 | 4.6 | 4.3 | 3.6 | 19,400 | 17,500 to 21,200 | 36 | 18,200 | 16,400 to 19,900 | 36 | 10,300 | 8,900 to 12,200 | 36 | +1.6 | −5.7 | −7.2 | −6.2 | −46.9 |
| | 24 | .88 | 22.3 | 1.1 | 2.1 | 4.5 | 4.0 | 3.4 | 18,800 | 16,200 to 20,400 | 36 | 17,600 | 16,300 to 18,900 | 36 | 9,700 | 8,400 to 10,600 | 36 | −1.6 | −8.8 | −12.6 | −6.4 | −48.4 |
| | 32 | .90 | 24.1 | 0.8 | 1.7 | 4.1 | 3.8 | 3.5 | 18,700 | 17,300 to 21,000 | 36 | 17,100 | 15,100 to 18,200 | 36 | 10,000 | 9,100 to 11,100 | 36 | −2.1 | −11.4 | −9.9 | −8.6 | −46.5 |
| | 64 | .92 | 24.6 | .3 | 1.5 | 3.9 | 3.6 | 3.4 | 18,100 | 12,500 to 20,000 | 36 | 15,000 | 13,700 to 17,200 | 36 | 8,600 | 6,500 to 9,700 | 36 | −5.2 | −22.3 | −22.5 | −17.1 | −52.5 |
| Sulfuric acid | 19 | .91 | 24.6 | 4.8 | 4.3 | 4.5 | 4.1 | 3.1 | 19,100 | 17,500 to 21,300 | 36 | 18,200 | 16,300 to 19,700 | 36 | 10,000 | 8,600 to 11,100 | 36 | 0.0 | −5.7 | −9.9 | −4.7 | −47.6 |
| | 24 | .88 | 21.7 | 2.4 | 3.1 | 4.2 | 4.1 | 3.2 | 19,400 | 17,100 to 22,000 | 36 | 18,700 | 16,500 to 20,000 | 36 | 10,200 | 9,100 to 11,800 | 36 | +1.6 | −3.1 | −8.1 | −3.6 | −47.4 |
| | 43 | .90 | 23.7 | 0.9 | 1.7 | 3.3 | 3.1 | 3.4 | 18,400 | 16,100 to 20,400 | 36 | 16,800 | 14,200 to 18,500 | 36 | 8,300 | 7,000 to 9,400 | 36 | −3.7 | −13.0 | −25.2 | −8.7 | −54.9 |
| | 72 | .90 | 22.5 | .4 | 1.5 | 2.4 | 2.5 | 3.4 | 18,000 | 14,200 to 20,400 | 36 | 14,100 | 11,200 to 15,900 | 36 | 8,500 | 6,800 to 10,400 | 36 | −5.8 | −26.9 | −23.4 | −21.7 | −52.8 |
| Phosphoric acid | 19 | .89 | 23.3 | 4.8 | 4.2 | 4.7 | 4.2 | 3.4 | 18,800 | 17,000 to 20,800 | 36 | 18,500 | 17,100 to 20,400 | 36 | 10,400 | 9,100 to 11,700 | 36 | −1.6 | −4.1 | −6.3 | −1.6 | −44.7 |
| | 24 | .88 | 22.7 | 2.9 | 3.0 | 4.5 | 4.1 | 3.4 | 18,300 | 16,900 to 19,800 | 36 | 17,900 | 15,300 to 19,400 | 36 | 10,000 | 8,100 to 11,200 | 36 | −4.2 | −7.2 | −9.9 | −2.2 | −45.4 |
| | 51 | .90 | 24.7 | 1.7 | 2.0 | 3.0 | 2.9 | 3.2 | 18,100 | 16,300 to 19,300 | 36 | 16,300 | 13,500 to 17,900 | 36 | 9,700 | 7,000 to 11,600 | 36 | −5.2 | −15.5 | −12.6 | −9.9 | −46.4 |
| | 101 | .96 | 28.7 | 1.1 | 1.9 | 2.4 | 2.5 | 3.6 | 18,800 | 13,800 to 20,400 | 36 | 13,600 | 12,000 to 15,600 | 36 | 8,700 | 7,900 to 9,600 | 36 | −6.8 | −29.5 | −23.4 | −23.6 | −51.1 |
| Hypophosphorous acid | 20 | .87 | 24.4 | 3.8 | 4.0 | 4.5 | 4.3 | 3.5 | 19,500 | 16,000 to 21,500 | 36 | 18,600 | 17,100 to 22,000 | 36 | 10,900 | 9,400 to 12,300 | 36 | +2.1 | −2.6 | −1.8 | −3.6 | −44.1 |
| | 27 | .88 | 24.2 | 2.4 | 2.7 | 4.2 | 4.1 | 3.4 | 19,100 | 17,900 to 20,100 | 36 | 18,300 | 16,200 to 19,500 | 36 | 10,600 | 9,100 to 12,400 | 36 | 0.0 | −5.2 | −4.5 | −4.2 | −44.5 |
| | 51 | .89 | 24.5 | 1.7 | 1.8 | 3.8 | 3.5 | 3.3 | 19,100 | 17,600 to 20,500 | 36 | 17,600 | 15,800 to 19,000 | 36 | 10,700 | 8,300 to 12,300 | 72 | .0 | −8.8 | −4.1 | −7.8 | −45.5 |
| | 100 | .91 | 24.1 | 1.4 | 1.6 | 2.6 | 2.8 | 3.5 | 18,800 | 17,500 to 20,100 | 36 | 15,800 | 13,900 to 18,200 | 36 | 9,000 | 6,400 to 12,400 | 35 | −1.6 | −18.1 | −18.9 | −16.0 | −52.1 |
| Benzenesulfonic acid | 19 | .86 | 21.3 | 4.4 | 4.2 | 4.5 | 4.3 | 3.1 | 19,400 | 18,000 to 20,800 | 36 | 18,200 | 17,100 to 19,500 | 36 | 10,200 | 7,400 to 12,400 | 36 | +1.6 | −5.7 | −8.1 | −6.2 | −47.4 |
| | 24 | .87 | 22.3 | 1.3 | 2.7 | 4.2 | 4.1 | 3.2 | 20,100 | 17,900 to 21,300 | 36 | 18,800 | 17,000 to 20,400 | 36 | 10,600 | 9,500 to 12,400 | 36 | +5.2 | −2.6 | −4.5 | −6.5 | −47.3 |
| | 32 | .89 | 23.6 | 0.8 | 1.9 | 3.8 | 3.7 | 3.1 | 19,600 | 17,400 to 20,400 | 36 | 17,800 | 14,800 to 19,900 | 36 | 9,500 | 8,200 to 11,300 | 36 | +2.6 | −7.8 | −14.4 | −9.2 | −51.5 |
| | 64 | .90 | 21.6 | .5 | 1.4 | 3.1 | 3.2 | 3.2 | 18,900 | 17,200 to 20,200 | 36 | 15,600 | 13,200 to 17,700 | 36 | 9,400 | 7,200 to 12,100 | 36 | −1.0 | −19.2 | −15.3 | −17.5 | −50.3 |
| Trichloroacetic acid | 21 | .87 | 20.5 | 2.8 | 4.0 | 5.7 | 5.0 | 3.8 | 18,700 | 16,900 to 20,500 | 36 | 18,200 | 16,300 to 20,200 | 36 | 10,700 | 9,700 to 11,600 | 36 | −2.1 | −5.7 | −3.6 | −2.7 | −42.8 |
| | 27 | .86 | 20.4 | 1.6 | 2.7 | 5.5 | 5.0 | 3.7 | 19,200 | 17,600 to 20,800 | 36 | 18,600 | 17,300 to 20,800 | 36 | 10,800 | 10,200 to 11,600 | 36 | +0.5 | −3.6 | −2.7 | −3.1 | −43.8 |
| | 43 | .85 | 21.0 | 1.2 | 1.6 | 5.3 | 5.1 | 3.7 | 18,500 | 15,800 to 20,000 | 36 | 16,900 | 14,900 to 18,800 | 36 | 10,300 | 9,000 to 11,000 | 36 | −3.1 | −12.4 | −7.2 | −8.6 | −44.3 |
| | 85 | .89 | 21.5 | 1.0 | 1.4 | 5.0 | 4.7 | 4.1 | 19,300 | 16,700 to 21,100 | 36 | 16,500 | 13,100 to 18,900 | 36 | 10,300 | 9,300 to 11,400 | 36 | +1.0 | −14.5 | −7.2 | −14.5 | −46.6 |
| Nitranilic acid | 21 | .86 | 21.3 | 5.5 | 4.6 | 5.0 | 4.8 | 3.4 | 18,800 | 13,800 to 21,100 | 36 | 18,400 | 15,400 to 21,400 | 36 | 10,100 | 9,000 to 11,600 | 36 | −1.6 | −4.7 | −9.0 | −2.1 | −46.3 |
| | 32 | .88 | 21.8 | 1.1 | 3.0 | 4.4 | 4.0 | 3.4 | 18,600 | 14,600 to 20,100 | 36 | 17,900 | 15,400 to 20,200 | 36 | 10,000 | 8,600 to 12,000 | 36 | −2.6 | −7.2 | −10.9 | −3.8 | −46.2 |
| | 45 | .87 | 22.2 | 0.7 | 2.7 | 4.1 | 3.9 | 3.3 | 18,200 | 16,400 to 20,300 | 36 | 16,700 | 15,200 to 17,700 | 36 | 9,300 | 7,700 to 11,200 | 34 | −4.7 | −13.5 | −16.2 | −8.2 | −48.9 |
| Sodium hydroxide | 440 | 1.08 | 35.3 | 10.5 | 11.5 | 9.2 | 8.5 | ------ | 19,200 | 16,900 to 21,500 | 30 | 16,000 | 14,300 to 18,000 | 30 | ------ | ------ | ------ | +0.5 | −17.1 | ------ | −16.7 | ------ |

[a] All panels prepared by pressing at 150° F for 24 hours, using metal bars to control thickness.

[b] Change in strength for the unaged and oven-fog-aged panels, respectively, is calculated on the basis of the strength of the unaged and oven-fog-aged panels, respectively, made without catalyst.

[c] Change in strength calculated on the basis of the strength of the unaged panel.

TABLE 10.—*Effect of alkali and acids on phenolic resin-bonded plywood* [a]

| Catalyst added to resin | Milliequivalents of catalyst per 100 g of resin | Density of panel | pH | | | | | Flexural strength data | | | | | | | | | Change in strength due to catalyst [b] | | | Change in strength due to aging [c] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Unaged panels | | | Oven-fog-aged panels | | | Roof-aged panels | | | | | | | |
| | | | | | | | | Flexural strength | | No. of specimens | Flexural strength | | No. of specimens | Flexural strength | | No. of specimens | | | | | |
| | | | Resin solution | Resin film | Unaged panel | Oven-fog-aged panel | Roof-aged panel | Average | Range | | Average | Range | | Average | Range | | Unaged panel | Oven-fog-aged panel | Roof-aged panel | Oven-fog-aged panel | Roof-aged panel |
| **CASCOPHEN LT-67 AND M-18** | | | | | | | | | | | | | | | | | | | | | |
| | | *g/cm³* | | | | | | *lb/in.²* | *lb/in.²* | | *lb/in.²* | *lb/in.²* | | *lb/in.²* | *lb/in.²* | | *Percent* | *Percent* | *Percent* | *Percent* | *Percent* |
| None | | 0.98 | 8.5 | 8.7 | 6.7 | 6.4 | 5.2 | 22,100 | 18,700 to 24,000 | 36 | 24,000 | 21,400 to 28,400 | 36 | 13,000 | 11,700 to 15,000 | 36 | | | | +8.6 | −41.2 |
| Sodium hydroxide | 460 | 1.03 | 12.1 | 12.2 | 8.6 | 8.2 | 5.7 | 22,100 | 19,500 to 24,000 | 36 | 18,800 | 17,300 to 20,500 | 36 | 13,900 | 11,900 to 15,200 | 36 | 0.0 | −21.7 | +6.9 | −14.9 | −37.1 |
| | 230 | 0.95 | 11.3 | 11.0 | 8.3 | 7.8 | 6.1 | 21,800 | 18,700 to 23,800 | 36 | 19,700 | 17,200 to 21,800 | 36 | 14,300 | 12,400 to 16,300 | 36 | −1.4 | −17.9 | +10.0 | −9.6 | −34.4 |
| | 105 | .98 | 10.0 | 10.4 | 7.6 | 7.7 | 5.7 | 21,800 | 20,100 to 23,800 | 36 | 20,400 | 17,900 to 21,800 | 36 | 13,500 | 12,000 to 14,700 | 36 | −1.4 | −15.0 | +3.8 | −6.4 | −38.1 |
| | 33 | .97 | 9.3 | 10.0 | 7.2 | 6.9 | 5.5 | 21,300 | 18,900 to 23,500 | 36 | 20,500 | 19,000 to 22,000 | 36 | 12,900 | 11,800 to 15,500 | 36 | −3.6 | −14.6 | −0.8 | −3.8 | −25.4 |
| Trichloracetic acid | 41 | .94 | 5.5 | 5.3 | 6.5 | 6.6 | 4.5 | 21,600 | 18,700 to 23,400 | 36 | 22,200 | 18,300 to 24,500 | 36 | 12,200 | 10,900 to 13,900 | 36 | −5.0 | −7.5 | −6.2 | +5.7 | −41.9 |
| | 49 | .92 | 2.1 | 4.4 | 6.5 | 6.4 | 5.0 | 20,200 | 16,700 to 23,300 | 36 | 20,900 | 18,700 to 23,700 | 36 | 11,800 | 9,400 to 14,400 | 36 | −8.6 | −12.9 | −10.8 | +3.5 | −42.6 |
| | 64 | .89 | 1.5 | 1.7 | 4.7 | 6.3 | 4.6 | 19,500 | 16,800 to 22,400 | 36 | 20,500 | 18,400 to 22,000 | 36 | 12,700 | 11,100 to 14,000 | 36 | −11.8 | −14.6 | −2.3 | +5.1 | −34.9 |
| | 39 | .92 | 6.2 | 5.6 | 4.7 | 4.5 | ..... | 21,200 | 19,000 to 24,900 | 48 | 21,200 | 18,700 to 23,600 | 42 | ..... | ..... | ..... | −4.1 | −11.7 | ..... | 0.0 | ..... |
| Benzenesulfonic acid | 45 | .90 | 3.1 | 4.1 | 4.4 | 4.2 | ..... | 20,400 | 18,300 to 23,500 | 48 | 20,700 | 18,500 to 22,800 | 42 | ..... | ..... | ..... | −7.7 | −13.8 | ..... | +1.5 | ..... |
| | 61 | .87 | 0.8 | 2.2 | 3.4 | 3.5 | ..... | 17,900 | 15,300 to 21,400 | 48 | 17,400 | 15,600 to 19,400 | 42 | ..... | ..... | ..... | −19.0 | −27.5 | ..... | −2.8 | ..... |
| | 43 | 1.04 | 6.4 | 5.6 | 4.6 | 4.0 | ..... | 24,200 | 20,800 to 26,100 | 48 | 22,700 | 21,300 to 24,800 | 42 | ..... | ..... | ..... | +9.5 | −5.4 | ..... | −6.2 | ..... |
| Hypophosphorous acid | 58 | 1.06 | 2.7 | 2.6 | 3.9 | 3.6 | ..... | 25,000 | 22,200 to 28,000 | 48 | 23,700 | 21,400 to 25,900 | 42 | ..... | ..... | ..... | +13.1 | −1.2 | ..... | −5.2 | ..... |
| | 116 | 0.94 | 1.9 | 1.6 | 2.2 | 2.1 | ..... | 19,700 | 17,700 to 22,200 | 48 | 13,600 | 11,600 to 14,500 | 42 | ..... | ..... | ..... | −10.9 | −43.3 | ..... | −31.0 | ..... |
| **DUREZ 12041** | | | | | | | | | | | | | | | | | | | | | |
| None | | 1.02 | 7.1 | 8.1 | 4.9 | 4.8 | ..... | 26,800 | 21,500 to 29,600 | 48 | 24,700 | 20,900 to 27,000 | 42 | ..... | ..... | ..... | | | | −7.8 | ..... |
| Hypophosphorous acid | 43 | 0.99 | 2.1 | 1.9 | 3.4 | 3.4 | ..... | 21,500 | 18,000 to 24,500 | 48 | 19,700 | 15,900 to 23,200 | 42 | ..... | ..... | ..... | −19.8 | −30.2 | ..... | −8.4 | ..... |
| | 58 | 1.02 | 2.3 | 1.8 | 3.1 | 2.5 | ..... | 23,500 | 20,000 to 26,600 | 48 | 22,200 | 19,000 to 24,400 | 42 | ..... | ..... | ..... | −12.3 | −10.1 | ..... | −5.5 | ..... |
| | 116 | 0.94 | 1.2 | 1.3 | 2.2 | 2.2 | ..... | 19,400 | 16,400 to 21,300 | 48 | 15,800 | 13,600 to 19,100 | 42 | ..... | ..... | ..... | −27.6 | −36.0 | ..... | −18.6 | ..... |

[a] All panels prepared by pressing at 150° F for 24 hours, using metal bars to control thickness.

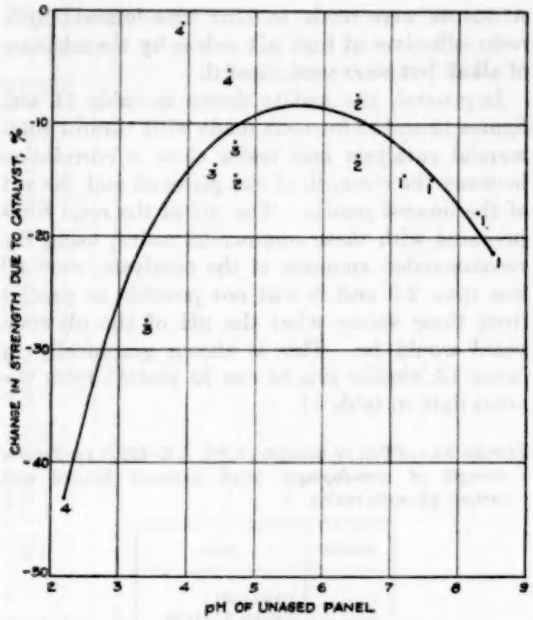
[b] Change in strength for the unaged, oven-fog-aged, and roof-aged panels, respectively, is calculated on the basis of the strength of the unaged, oven-fog-aged, and roof-aged panels, respectively, made without catalyst.

[c] Change in strength calculated on the basis of the strength of the unaged panel.

The Cascophen LT–67 resin was also treated h various amounts of sodium hydroxide, a g base. No evidence of significant deteriora- in strength of the unaged plywood by rela- ly large amounts of the alkali was noted. How- r, there was some decrease in strength when plywood was exposed to oven-fog aging condi- s. The decrease in strength correlated with ease in pH from an initial value of 6.4 for the d panel without added alkali to 8.2 for the aged el with the greatest amount of added alkali.

URE 11.—*Effect of various catalysts on flexural strength oven-fog-aged birch plywood bonded with Cascophen T-67.*

| Sample | Catalyst |
|---|---|
| 1 | Sodium hydroxide |
| 2 | Trichloroacetic acid |
| 3 | Benzenesulfonic acid |
| 4 | Hypophosphorous acid |



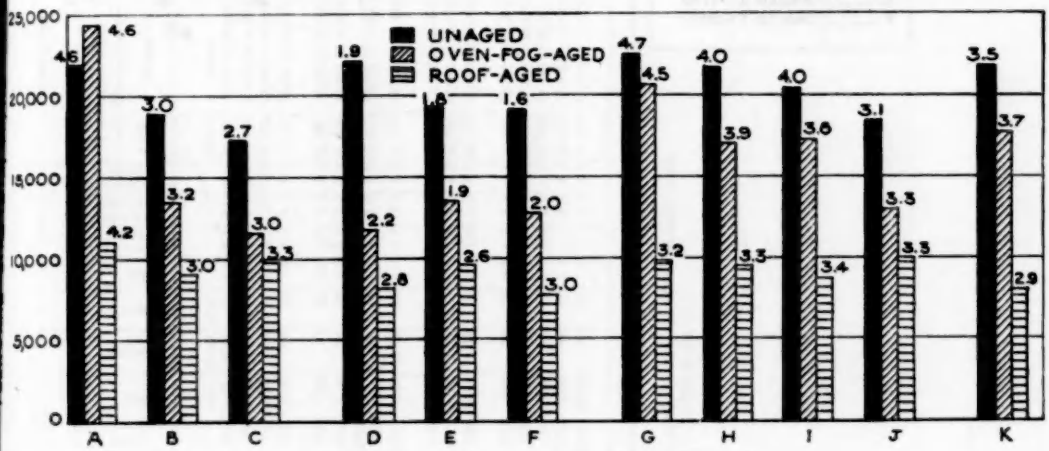




FIGURE 12.—*Effect of various catalysts on flexural strength of birch plywood bonded with phenolic resins. (Number above each column indicates* pH *value of unaged panel.)*

| Sample | Resin | Catalyst |
|---|---|---|
| A | Durez 12041 | 3.2% Bakelite XK–2997. |
| B | Bakelite XC–11749 | Do. |
| C | Bakelite XC–3931 | Do. |
| D | Bakelite XC–11749 | 10% Durez 7422. |
| E | Durez 12041 | Do. |
| F | Bakelite XC–3931 | Do. |
| G | Bakelite XC–11749 | 5% Bakelite XK–11753. |
| H | do | 20% Bakelite XK–11753. |
| I | do | 30% Bakelite XK–11753. |
| J | do | 45% Bakelite XK–11753. |
| K | Bakelite XC–3931 | 45% Bakelite XK–11753. |

Attempts were made to cure urea-formaldehyde resin adhesives at high pH values by the addition of alkali but were unsuccessful.

In general, the results shown in table 11 and figures 12 and 13 for tests made with various commercial catalysts and resins show a correlation between the strength of the plywood and the pH of the unaged panels. The pH of the resin films prepared with these commercial resins, using the recommended amounts of the catalysts, were all less than 2.0 and it was not possible to predict from these values what the pH of the plywood panel would be. This is shown graphically in figure 13; similar graphs can be plotted from the other data in table 11.

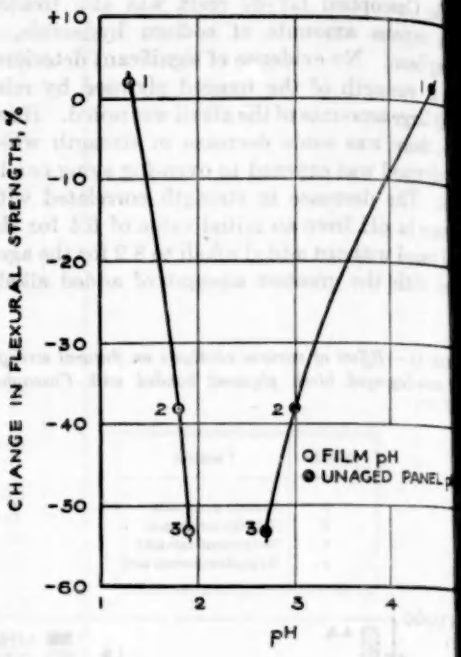



FIGURE 13.—*Effect of catalyst (3.2% XK–2997) on flexural strength of oven-fog-aged birch plywood bonded with various phenolic resins.*

| Sample | Resin |
|---|---|
| 1 | Durez 12041. |
| 2 | Bakelite XC–11749. |
| 3 | Bakelite XC–3931. |

| Commercial designation of resin | Catalyst added to resin | Classification | Conditions of cure: Temperature | Conditions of cure: Time | Density | Resin content | pH: Film | pH: Unaged panel | pH: Oven-fog-aged panel | pH: Roof-aged panel | Unaged panel: Flexural strength: Average | Unaged panel: Flexural strength: Range | Unaged panel: No. of specimens | Oven-fog-aged panel: Flexural strength: Average | Oven-fog-aged panel: Flexural strength: Range | Oven-fog-aged panel: No. of specimens | Roof-aged panel: Flexural strength: Average | Roof-aged panel: Flexural strength: Range | Roof-aged panel: No. of specimens | Change in strength due to catalyst [a]: Unaged panel | Change in strength due to catalyst [a]: Oven-fog-aged panel | Change in strength due to catalyst [a]: Roof-aged panel | Change in strength due to aging [b]: Oven-fog-aged panel | Change in strength due to aging [b]: Roof-aged panel |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | °F | hr: min | g/cm³ | Per cent | | | | | lb/in.² | lb/in.² | | lb/in.² | lb/in.² | | lb/in.² | lb/in.² | | Per cent | Per cent | Per cent | Per cent | Per cent |
| Bakelite XC-11749 | None | H | 300 | 0:45 | 0.94 | 26 | 5.9 | 4.8 | 4.4 | 3.7 | 24,600 | 22,100 to 26,800 | 15 | 21,900 | 18,300 to 24,100 | 15 | 14,200 | 11,500 to 16,000 | 15 | | | −11 | −42 | |
| | 45% XK-11753 | R | Room | 20:00 | .88 | 31 | 1.9 | 3.1 | 3.3 | 3.3 | 18,400 | 15,400 to 19,700 | 12 | 12,900 | 8,700 to 15,300 | 12 | 9,800 | 6,000 to 11,400 | 12 | −25 | −41 | −31 | −30 | −47 |
| | 3.2% XK-2997 | M | 150 | 20:00 | .94 | 29 | 1.8 | 3.0 | 3.2 | 3.0 | 18,800 | 15,600 to 23,000 | 16 | 13,500 | 11,600 to 16,400 | 16 | 9,000 | 6,000 to 11,000 | 16 | −24 | −38 | −37 | −28 | −52 |
| | 10% Durez 7422 | M | 150 | 20:00 | .95 | 31 | 1.4 | 1.9 | 2.2 | 2.8 | 22,100 | 19,900 to 23,600 | 16 | 11,800 | 9,400 to 13,400 | 16 | 8,200 | 6,500 to 9,100 | 16 | −10 | −46 | −42 | −47 | −63 |
| Bakelite XC-3931 | None | H | 300 | 0:30 | .97 | 35 | 5.5 | 4.5 | 4.5 | 3.5 | 23,600 | 18,100 to 30,000 | 15 | 24,800 | 23,300 to 26,300 | 15 | 10,700 | 9,100 to 12,800 | 15 | | | | +5 | −55 |
| | 45% XK-11753 | M | 150 | 20:00 | .94 | 35 | 1.9 | 3.5 | 3.7 | 2.9 | 21,800 | 19,400 to 25,800 | 16 | 17,700 | 14,300 to 20,600 | 16 | 8,000 | 7,100 to 9,800 | 16 | −8 | −29 | −25 | −19 | −63 |
| | 3.2% XK-2997 | M | Room / 150 | 20:00 / 2:00 | .90 | 31 | 1.9 | 2.7 | 3.0 | 3.3 | 17,300 | 15,200 to 19,900 | 12 | 11,600 | 8,800 to 13,600 | 12 | 9,800 | 4,900 to 11,500 | 12 | −27 | −53 | −8 | −33 | −43 |
| | 10% Durez 7422 | R | Room | 20:00 | 1.02 | 43 | 1.2 | 1.6 | 2.0 | 3.0 | 18,100 | 16,700 to 19,200 | 16 | 12,800 | 11,000 to 14,000 | 16 | 7,800 | 6,900 to 9,200 | 16 | −23 | −48 | −27 | −29 | −57 |
| Durez 12041 [c] | None | H | 300 | 0:30 | 0.97 | 33 | 8.2 | 5.0 | 5.0 | 4.7 | 24,700 | 22,400 to 28,700 | 15 | 23,800 | 21,300 to 27,100 | 15 | 17,800 | 15,300 to 21,000 | 15 | | | | −4 | −29 |
| | 3.2% XK-2997 | R | Room | 20:00 | 1.02 | 34 | 1.3 | 4.6 | 4.6 | 4.2 | 21,800 | 19,900 to 24,800 | 16 | 24,300 | 18,800 to 27,700 | 16 | 11,000 | 7,300 to 14,500 | 16 | −12 | +2 | −38 | +11 | −50 |
| | 10% Durez 7422 | M | 150 | 24:00 | 0.97 | 36 | 1.4 | 1.8 | 1.9 | 2.6 | 19,400 | 17,300 to 20,600 | 12 | 13,500 | 10,100 to 15,300 | 12 | 9,600 | 8,400 to 10,900 | 12 | −21 | −43 | −46 | −30 | −51 |
| Bakelite XC-11749 | None | H | 300 | 0:45 | .94 | 26 | 5.9 | 4.8 | 4.4 | 3.7 | 24,600 | 22,100 to 26,800 | 15 | 21,900 | 18,300 to 24,100 | 15 | 14,200 | 11,500 to 16,000 | 15 | | | | −11 | −42 |
| | 5% XK-11753 | M | 150 | 20:00 | .93 | 27 | 4.2 | 4.7 | 4.5 | 3.2 | 22,600 | 20,900 to 24,500 | 16 | 20,700 | 17,600 to 22,900 | 16 | 9,800 | 8,700 to 10,800 | 16 | −8 | −5 | −31 | −8 | −57 |
| | 20% XK-11753 | M | 150 | 3:00 | .89 | 27 | 2.3 | 4.0 | 3.9 | 3.3 | 21,700 | 18,700 to 24,300 | 16 | 17,000 | 12,700 to 20,100 | 16 | 9,400 | 7,100 to 11,400 | 16 | −12 | −22 | −34 | −22 | −57 |
| | 30% XK-11753 | M | 150 | 3:00 | .89 | 27 | 2.2 | 4.0 | 3.8 | 3.4 | 20,400 | 17,300 to 22,800 | 16 | 17,200 | 15,100 to 19,800 | 16 | 8,700 | 7,300 to 9,700 | 16 | −17 | −21 | −39 | −16 | −57 |
| | 45% XK-11753 | R | Room | 20:00 | .88 | 31 | 1.9 | 3.1 | 3.3 | 3.3 | 18,400 | 15,400 to 19,700 | 12 | 12,900 | 8,700 to 15,300 | 12 | 9,800 | 6,000 to 11,400 | 12 | −25 | −41 | −31 | −30 | −47 |

[a] Change in strength for the unaged, oven-fog-aged, and roof-aged panels, respectively, is calculated on the basis of the strength of the unaged, oven-fog-aged, and roof-aged panels, respectively made without catalyst.

[b] Change in strength calculated on the basis of the strength of the unaged panel.

[c] This resin would not cure with catalyst XK-11753 at 150° F.

### 3. Effect of Acids and Bases on Wood

The marked decrease in strength of the unaged plywood panels which resulted generally throughout the experiments reported herein when the pH of the panels was lowered by acid catalysts indicated that the wood was being attacked by the acids. The data in table 12 and figure 14 indicate that both pH and catalyst radical have a part in this breakdown. Hydrochloric, benzenesulfo nitric, and sulfuric acids had the most pronou deteriorating effect on the birch wood. Nitra and hypophosphorous acids had considerably deteriorating action on the wood. This is part larly evident from a comparison of strengths the birch veneers treated with the respective a to produce pH conditions in the range 2.1 to

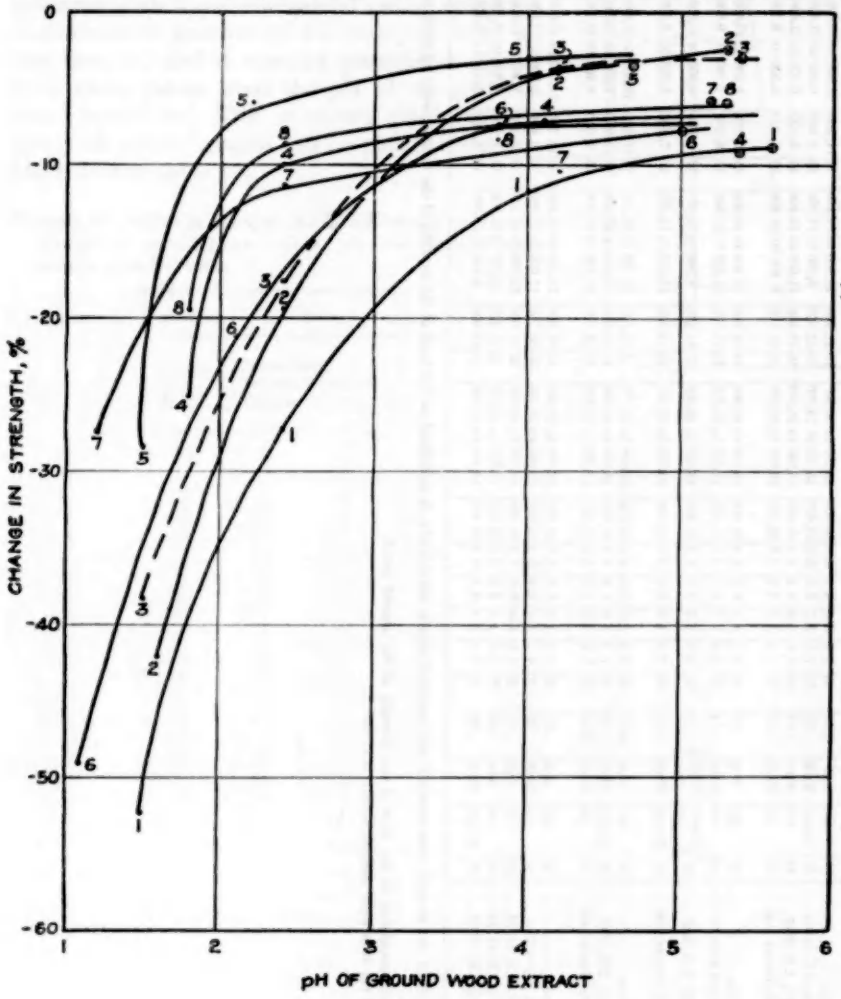



FIGURE 14.—*Effect of* var *acids on flexural streng birch wood*

| Sample | Acid |
|---|---|
| 0 | None (water trea only) |
| 1 | Hydrochloric |
| 2 | Nitric |
| 3 | Sulfuric |
| 4 | Phosphoric |
| 5 | Hypophosphorous |
| 6 | Benzenesulfonic |
| 7 | Trichloroacetic |
| 8 | Nitranilic |

narked decrease in strength occurred in every when the pH of the birch veneers was lowered w pH 2.0 by treatment with the respective is. The wood had a strong buffering action against alkalies. However, a pronounced decrease in strength occurred when the pH of the wood was raised to 8.8 by absorption of tetraethanolammonium hydroxide.

TABLE 12.—*Effect of catalysts on flexural strength of birch veneers* [a]

| Catalyst | Normality of solution | pH | | | Flexural strength data | | | |
|---|---|---|---|---|---|---|---|---|
| | | Original solution | Solution after wood immersion | Ground wood | Flexural strength | | No. of specimens | Loss in strength [b] |
| | | | | | Average | Range | | |
| | | | | | *lb/in.²* | *lb/in.²* | | *Percent* |
| | 1.0 | 0.12 | 0.03 | 1.5 | 9,800 | 8,600 to 12,800 | 10 | 52.2 |
| | 0.1 | 1.1 | 1.4 | 2.4 | 14,900 | 13,000 to 16,500 | 12 | 27.3 |
| chloric acid | .01 | 2.0 | 3.1 | 4.0 | 18,100 | 16,800 to 18,900 | 12 | 11.7 |
| | Water | 5.5 | 5.2 | 5.6 | 18,700 | 17,100 to 20,000 | 12 | 8.8 |
| | Untreated wood [a] | | | 6.0 | 20,500 | 19,100 to 22,700 | 12 | |
| | 1.0 | 0.1 | 0.21 | 1.6 | 12,300 | 10,800 to 13,800 | 12 | 42.0 |
| | 0.1 | 1.1 | 1.4 | 2.4 | 17,100 | 16,100 to 18,800 | 12 | 19.3 |
| ric acid | .01 | 2.0 | 3.4 | 4.2 | 20,400 | 18,900 to 22,700 | 12 | 3.8 |
| | Water | 5.5 | 4.9 | 5.3 | 20,700 | 18,900 to 22,200 | 12 | 2.4 |
| | Untreated wood | | | 5.8 | 21,200 | 19,100 to 22,900 | 12 | |
| | 1.0 | 0.33 | 0.34 | 1.5 | 12,300 | 10,700 to 13,400 | 12 | 38.2 |
| | 0.1 | 1.3 | 1.4 | 2.4 | 16,400 | 14,700 to 17,700 | 12 | 17.6 |
| ric acid | .01 | 2.1 | 3.1 | 4.2 | 19,200 | 17,800 to 20,800 | 12 | 3.5 |
| | Water | 5.6 | 5.5 | 5.4 | 19,300 | 18,500 to 20,400 | 12 | 3.0 |
| | Untreated wood | | | 5.5 | 19,900 | 18,900 to 21,600 | 12 | |
| | 3.0 | 0.8 | 0.88 | 1.8 | 15,000 | 13,900 to 16,700 | 12 | 25.0 |
| | 0.3 | 1.6 | 1.8 | 2.4 | 18,000 | 16,600 to 19,200 | 12 | 10.0 |
| sphoric acid | .03 | 2.2 | 3.2 | 4.1 | 18,600 | 15,600 to 20,100 | 12 | 7.0 |
| | Water | 5.5 | 6.0 | 5.4 | 18,500 | 16,800 to 20,800 | 12 | 9.2 |
| | Untreated wood | | | 5.5 | 20,000 | 17,600 to 23,400 | 12 | |
| | 1.0 | 0.6 | 0.72 | 1.5 | 14,700 | 12,900 to 16,900 | 12 | 28.3 |
| | 0.1 | 1.3 | 1.6 | 2.2 | 19,300 | 17,400 to 20,400 | 12 | 5.9 |
| yphosphorous acid | .01 | 2.2 | 3.1 | 4.0 | 19,900 | 18,900 to 20,700 | 12 | 2.9 |
| | Water | 5.5 | 5.2 | 4.7 | 19,800 | 18,100 to 20,300 | 12 | 3.4 |
| | Untreated wood | | | 4.9 | 20,500 | 19,500 to 21,200 | 12 | |
| | 1.0 | 0.1 | 0.18 | 1.1 | 10,400 | 9,600 to 11,300 | 12 | 49.0 |
| | 0.1 | 1.1 | 1.2 | 2.1 | 16,100 | 13,900 to 17,800 | 12 | 21.1 |
| nesulfonic acid | .01 | 2.0 | 3.2 | 3.8 | 18,900 | 16,900 to 20,400 | 12 | 7.4 |
| | Water | 5.5 | 5.4 | 5.0 | 18,800 | 17,300 to 21,000 | 12 | 7.8 |
| | Untreated wood | | | 4.9 | 20,400 | 18,900 to 22,700 | 12 | |
| | 1.1 | 0.1 | 0.56 | 1.2 | 14,000 | 12,400 to 15,100 | 12 | 27.5 |
| | 0.11 | 1.2 | 1.1 | 2.4 | 17,100 | 15,600 to 19,400 | 12 | 11.4 |
| hloroacetic acid | .01 | 2.1 | 2.7 | 4.2 | 17,300 | 15,400 to 19,100 | 12 | 10.4 |
| | Water | 5.9 | 5.0 | 5.2 | 18,200 | 16,500 to 20,200 | 12 | 5.7 |
| | Untreated wood | | | 5.3 | 19,300 | 17,000 to 21,400 | 12 | |
| | 1.0 | 0.42 | 0.80 | 1.8 | 16,600 | 15,500 to 17,800 | 12 | 19.4 |
| | 0.2 | 1.0 | 1.6 | 2.4 | 18,800 | 18,200 to 19,900 | 12 | 8.7 |
| cinilic acid | .02 | 1.9 | 2.7 | 3.8 | 18,900 | 18,100 to 20,400 | 12 | 8.2 |
| | Water | 5.5 | 5.0 | 5.3 | 19,400 | 17,700 to 20,000 | 12 | 5.8 |
| | Untreated wood | | | 5.8 | 20,600 | 19,700 to 21,200 | 12 | |
| | 0.1 | 12.9 | 10.2 | 7.0 | 20,200 | 18,700 to 22,300 | 12 | 6.0 |
| | .01 | 12.0 | 6.0 | 6.2 | 20,100 | 17,900 to 22,300 | 12 | 6.5 |
| dium hydroxide | Water | 5.8 | 5.0 | 5.4 | 20,100 | 18,800 to 21,700 | 12 | 6.5 |
| | Untreated wood | | | 5.7 | 21,500 | 20,700 to 22,400 | 12 | |
| | 0.44 | 12.4 | 11.7 | 8.8 | 16,300 | 12,800 to 17,900 | 12 | 20.1 |
| | .22 | 12.1 | 8.8 | 7.1 | 19,000 | 17,700 to 21,100 | 12 | 6.9 |
| traethanolammonium hydroxide | Water | 5.6 | 5.0 | 5.1 | 20,100 | 18,200 to 21,300 | 12 | 1.5 |
| | Untreated wood | | | 5.5 | 20,400 | 18,900 to 22,500 | 12 | |

[a] A birch veneer of 0.1-in. thickness was cut into the required number of specimens for treatment with a single catalyst. The specimens for immersion in d concentration of the catalyst for 3 days were selected so as to be representative of the whole veneer. Two similar sets of specimens from the same veneer n tested untreated and after immersion in distilled water for 3 days, respectively.

[b] The percentage loss in flexural strength is calculated on the basis of the strength of the untreated wood from the same veneer.

# VII. Conclusions

The flexural, impact and shear strengths, both initially and after aging, of urea and phenolic resin-bonded birch plywoods are definitely affected by the pH. In the acid range, the lower the pH of the plywood panel, the poorer is the strength of the panel and its resistance to aging. The lower critical pH value below which optimum strengths are not obtained and deterioration upon aging becomes appreciable, is approximately 4 for urea resin-bonded plywoods and 3.5 for phenolic resin-bonded plywoods. The decrease in strength on aging of birch plywood bonded with a phenolic resin catalyzed with a strong alkali (sodium hydroxide) correlated with increase in pH of the plywood. The upper critical pH values, above which optimum strengths are not obtained and deterioration upon aging becomes appreciable, appears to be in the neighborhood of 8 for phenolic resins; the value for urea resin-bonded plywoods was not established because the resins would not cure at the high pH values.

The delamination of birch plywoods made with urea-formaldehyde resins is affected by the pH; in the acid range, the lower the pH, the fewer cycles required for delamination to occur. The delamination of birch plywoods made with phenolic resin is not affected by the pH; when the pH is less than 3.1, the materials are not as flexible as those with pH values of 3.6 or more. In one-year roof-aging tests delamination occurred in the case of plywood bonded with casein with urea-formaldehyde resins containing catalysts which reduced the pH of the un panel to 3.4 or less.

At a given pH, strong acids, such as hy chloric, nitric, and sulfuric acids, had only sli greater deteriorating action on resorcinol-for dehyde resin-bonded birch plywood than did weaker types, such as hypophosphorous nitranilic acids.

The pH values of the birch plywoods made w various resins are not markedly changed moderate heating (40 hours at 80° C), by posure to cycles of heat and fog or by expos outdoors for one year.

Both pH and the nature of the acid radical h an effect on the deterioration of birch wood acids. At a given pH weak acids have consi ably less deteriorating action on the wood than strong acids. A pronounced decrease in stren of birch wood occurred when the pH of birch w was raised to 8.8 by absorption of tetraetha ammonium hydroxide.

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# urification of Sodium Chloride and Potassium Chloride for Use in Electrochemical Work, and the Determination of Small Amounts of Bromide

*By Gladys D. Pinching and Roger G. Bates*

The effects of small amounts of dissolved impurities on the potentials of silver–silver-halide electrodes immersed in solutions of alkali halides were studied. Traces of bromide exert disturbing effects on the potential of the silver–silver-chloride electrode. A convenient method for determining small amounts of bromide in the presence of chlorides and a satisfactory means of purifying sodium and potassium chlorides for precise electrochemical work are outlined. The procedure involves treatment of a saturated solution of the salt with chlorine, two successive precipitations with hydrogen chloride, and fusion of the air-dried product. A method for diminishing hydrolysis of the salts during fusion is described.

## Effect of Dissolved Impurities on the Potentials of Silver–Silver-Halide Electrodes Immersed in Solutions of Alkali Halides

mall amounts of bromide are known to exert rge effect on the potentials of the saturated mel electrod [1][1] and the silver–silver-chloride trode [2, 3]. Sodium chloride and potassium ride, sufficiently pure for many physicochemi- purposes, may, because of the presence of ll amounts of bromide, be quite unsuitable the most precise electrometric work. A series emf measurements was made to obtain ntitative information regarding this effect and scertain whether some of the other common urities have a similar disturbing influence.

### 1. Experimental Procedures

ell vessels of a modified H-type were used· two arms of each cell were separated by a pcock with a 5-mm bore. Each arm could be d and emptied by use of pure hydrogen without introduction of air. Two electrodes were used ach arm of the cell.

ilver–silver-chloride electrodes of the thermal-trolytic type [4, type 2] were used. Silver–

[1] Figures in brackets indicate the literature references at the end of this paper.

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silver-bromide electrodes were made as outlined by Keston [5], except that the mixture of silver oxide and silver bromate was decomposed at 550° C instead of 650° C. Silver–silver-iodide electrodes were prepared by the thermal decomposition, at 450° to 500° C, of a paste composed of 90 percent of silver oxide and 10 percent of silver iodide by weight, a method suggested earlier by one of the authors [6]. Bromide-free sodium chloride, potassium chloride, and hydrochloric acid were used for the tests. Sodium bromide was recrystallized three times from water, separated from its saturated solution by a filter of sintered glass, and dried at 200° to 250° C [4]. Other salts were of regeant grade.

The electrodes were brought to equilibrium in the solution of the pure halide, and those which differed from the mean potential by more than 0.1 mv were rejected. Silver–silver-iodide electrodes often differed by several tenths of a millivolt until hydrogen was bubbled through the solution to remove air.

Each cell was filled with two carefully deaerated portions of the halide solution, to one of which a small quantity of foreign salt (amounting to 0.05 to 0.5 mole per 100 moles of halide) had been added. Each arm was usually filled two or three times and the solution displaced with pure hydrogen before the final filling of the cell. The stopcock was open only while measurements were being made. In one experiment, the stopcock that separated 0.05-*M* hydrochloric acid from a solution 0.05 *M* in hydrochloric acid and 0.000025 *M* in potassium bromide was left open for 2 days. The constancy of $\Delta E$ during this time indicated that little if any bromide reached the silver–silver-chloride electrodes in the pure solution of hydrochloric acid.

The results are summarized in table 1; $\Delta E$ represents the average difference, in millivolts, between the electrodes in the pure and contaminated halide solutions. In general, $\Delta E$ reached a constant value within an hour. When silver–silver-chloride electrodes were immersed in solutions that contained bromide, or silver–silver-bromide electrodes in solutions containing iodide as an impurity, the electromotive force rose slowly for 24 to 48 hours, and sometimes measurement was discontinued before a limit was reached. The lower value of $\Delta E$ in the table usually represents the electromotive force about 1 hour after the cell was filled, and the higher the constant value that recorded 24 hours later.

TABLE 1.—*Effect of small concentrations of foreign salts on the potentials of silver–silver-halide electrodes immersed in solutions of halides at 25° C*

| Foreign salt | Molality of— | | Mole percentage of foreign salt | $\Delta E$ [a] |
|---|---|---|---|---|
| | Halide | Foreign salt | | |
| **Ag-AgCl electrodes in NaCl solutions** | | | | |
| | | $\times 10^3$ | | |
| KBr | 0.02 | 1.3 | 0.064 | 0.07 |
| | .05 | 25 | .5 | |
| KI | .05 | 2.5 | .05 | |
| | .05 | 5 | .1 | |
| | .05 | 25 | .5 | |
| KCN | .05 | 2.5 | .05 | |
| $Na_2SO_4$ | .05 | 5 | .1 | |
| $Na_2C_2O_4$ | .02 | 1 | .05 | |
| $Na_2HPO_4$ | .02 | 1 | .05 | |
| $Na_2S$ | .05 | 2.5 | .05 | |
| | .05 | 25 | .5 | |
| **Ag-AgCl electrodes in KCl solutions** | | | | |
| KBr | 0.05 | 2.5 | 0.05 | .7 |
| | .05 | 6 | .12 | |
| | 4.83 | 241 | .05 | |
| **Ag-AgCl electrodes in HCl solutions** | | | | |
| KBr | 0.05 | 2.5 | 0.05 | 0.46 |
| **Ag-AgBr electrodes in NaBr solutions** | | | | |
| KCl | 0.05 | 25 | 0.5 | |
| KI | .05 | 25 | .5 | [b] 2.22 to |
| **Ag-AgI electrodes in KI solutions** | | | | |
| NaCl | 0.05 | 2.5 | 0.05 | |
| KBr | .05 | 2.5 | .05 | |

[a] Positive $\Delta E$ signifies that the electrodes in the solution of impure were negative with respect to those in the solution of the pure halide.
[b] Electrodes in the iodide solution were yellow at the end of the experi
[c] Electrodes in the sulfide solution were black at the end of the experi
[d] Reference [3].

## Calculation of the Normal Effect of Impurities

When the impurity forms neither stable complex ions with silver nor compounds less soluble than silver chloride, $\Delta E$ is given by

$$\Delta E = \frac{RT}{F} \ln \frac{a_{Cl}}{a'_{Cl}} \pm E_j, \qquad (1)$$

where $a$ is the activity; $R$, $T$, and $F$ are the gas constant, the absolute temperature, and the faraday, respectively, and $E_j$ is the potential difference across the liquid junction in the stopcock. As the concentration of chloride ion is the same in both solutions, eq 1 becomes, with the substitution of numerical values for $R$, $T$, and $F$ at 25°C and conversion to the common logarithm,

$$\Delta E = 0.05914 \log (f_{Cl}/f'_{Cl}) \pm E_j, \qquad (2)$$

where $f$ is the activity coefficient of chloride ion on the molal scale. The difference in the activity coefficient caused by the difference in the ionic strengths of the two solutions can be estimated by use of one of the forms of the Debye-Hückel equation. When 0.5 mole percent of uni-univalent salt has been added to 0.05-$m$ sodium chloride, the ionic strength is increased from 0.05 to 0.05025, and the first term on the right of eq 1 is only 0.01 mv. The value of the liquid-junction potential cannot readily be estimated. In spite of the fact that the solutions on either side of the stopcock are practically identical in composition, $E_j$ is possibly large enough to mask the small effect of the change in the activity coefficient.

When certain impurities, such as iodide, are present, even in small concentrations, a silver salt of lower solubility than silver chloride may be formed on the surface of the electrode. From a comparison of the solubility product constants of silver chloride and silver iodide it is easily seen that practically all of the iodide impurity in the immediate vicinity of a silver chloride electrode is replaced by chloride ion, according to the reaction

$$AgCl + I^- = AgI + Cl^-. \qquad (3)$$

In a 0.05-$m$ solution of sodium chloride, originally containing 0.00025-$m$ potassium iodide, the concentration of iodide remaining at equilibrium with the electrode is only $10^{-8}$ $m$. Thus a concentration cell has been created, with chloride ion in the two arms at molalities of 0.05 and 0.05025. The emf of such a cell at 25° C is given by

$$\Delta E = \frac{T_{Na} \Delta \mu_{NaCl}}{F} = 0.1183 T_{Na} \log \frac{f'm'}{fm}. \qquad (4)$$

where $\mu$ is the partial molal free energy, or "chemical potential"; $m$ is the molality, and $f$ is the stoichiometrical activity coefficient of sodium chloride; and $T_{Na}$ is the transference number of sodium ion in 0.05-$m$ sodium chloride, found by Longsworth [7] to be 0.388 at 25° C. From eq 4, the potential of the electrode in the solution to which iodide was added should differ from that of the electrode in the pure solution of sodium chloride by 0.10 mv. The electrode immersed in the solution that contained potassium iodide was negative with respect to the other. This computed value agrees satisfactorily with 0.17 mv found by experiment.

The effect of sulfide ions likewise appears to be of this normal type, as 0.05 mole percent of this impurity, considerably more than necessary to exceed the solubility of silver sulfide, produces little if any abnormal effect. When the concentration of sulfide was increased tenfold, however, the electrodes were black in color and were negative to the reference pair by more than half a millivolt. It is possible that the formation of solid solutions is responsible for such a disturbance when deposition of a second silver salt in substantial amounts has occurred. In most cases this phenomenon is of less concern than the more obscure and equally harmful effect of bromide in concentrations insufficient to cause separation of silver bromide.

An accurate computation of the molality of bromide or iodide ion necessary to form solid silver bromide or silver iodide on the surface of a silver–silver-chloride electrode immersed in a solution of alkali chloride is perhaps most conveniently made with the aid of the standard potentials, $E°$, of the three silver–silver-halide electrodes, namely, −0.2224 (AgCl), −0.0713 (AgBr), and +0.1522 (AgI) int. v at 25° C. These standard potentials are related to the standard potential of the silver electrode, $E°_{Ag}$, and the solubility product constants, $K_{sp}$, of the respective silver halides, AgX, by the equation,

$$E°_{AgX} = E°_{Ag} - \frac{RT}{F} \ln K_{sp(AgX)} =$$

$$E°_{Ag} - 0.05914 \log f_{Ag} f_X m_{Ag} m_X. \qquad (5)$$

When the silver electrode is in equilibrium with a solution saturated with both silver chloride and silver bromide, we have, since $f_{Cl}$ and $f_{Br}$ are nearly equal,

$$E^{\circ}_{AgBr} - E^{\circ}_{AgCl} = 0.05914 \log (m_{Cl}/m_{Br}). \quad (6)$$

In this way, the value of $m_{Br}$ in equilibrium with solid silver bromide is found to be 0.00279 $m_{Cl}$, or 0.28 mole percent of the chloride. Similarly, $m_I = 4.63 \times 10^{-7}\ m_{Cl}$, or 0.00005 mole percent; and $m_I = 0.000166\ m_{Br}$ or 0.017 mole percent.

### 3. Anomalous Effect of Bromide on the Silver–Silver-Chloride Electrode

It can be concluded from table 1 that neither chloride nor bromide exerts a serious disturbing influence on the silver–silver-iodide electrode. Some difficulty was experienced, however, in obtaining reproducible results with iodide electrodes. Because both positive and negative values of $\Delta E$ were obtained, it seems likely that no abnormal effect of bromide exists. Deposition of silver iodide on the silver–silver-bromide electrode caused an abnormal potential difference of 2.2 mv, as compared with 0.10 mv calculated in the previous section.

Carmody [8] found that cyanide, absorbed during the electrolytic deposition of silver, was completely removed only after prolonged washing of the electrodes. The residual traces of cyanide effected some reduction of silver chloride during chloridization, and dark electrodes, positive to the white ones by about 0.2 mv, resulted. White electrodes were obtained only when the silver was washed for 2 weeks before the silver chloride was formed. As recorded in table 1, electrodes immersed in a 0.05-$m$ solution of sodium chlor that contained 0.05 mole percent of potassi cyanide were found to be negative to those in pure solution of chloride by 0.23 mv. The el trodes remained white. It seems likely that concentration of cyanide in the chloridizing would be less than 0.000025 $m$, the concentrat used in the experiment reported in table 1, wh the silvered electrode had been washed for onl few days. Apparently a greater disturbing eff results from the presence of cyanide in sm amounts during chloridization of the electro than from its presence as an impurity in solution in which the electrodes are used.

The potential of the silver–silver-chloride el trode is increased by 0.1 to 0.2 mv for each 0. mole percent of bromide. In one experimen the electrodes returned rapidly to substanti agreement when they were replaced in a bromid free solution of potassium chloride. The cause the abnormal effect of small amounts of bromi is as yet unexplained.

It has been found [1] that commercial sampl of potassium chloride often contain from 0.01 0.1 percent of bromide. In view of the magn tude of the error which these amounts wou cause, the removal of bromide becomes an im portant aspect of the purification of salt to b used in precise electrometric work. An investi gation was therefore undertaken to find a con venient test for the presence of bromide and t determine an efficient method for removing th impurity. Iodide appears to be absent from mos commercial preparations. In view of its rela tively small effect on the silver–silver-chlorid electrode, special treatment to remove iodide i probably unnecessary.

## II. Determination of Bromide in the Presence of Chloride

The formation of red eosin (tetrabromofluorescein) by the action of bromine on fluorescein has been utilized for the detection of small amounts of bromide [9]. The modification suggested by Aickin, in which the color was produced on test papers rather than in solution, appeared to be the most convenient. In this method a solution of fluorescein is prepared by stirring the dye in 50-percent ethyl alcohol for 30 minutes in the cold and removing the excess by filtration. Strips of filter paper are dipped into the solution, allowed to dry, and stored in the dark until needed. Two-tenths milliliter of a saturated aqueous solution of the salt to be tested is placed in a small test tube (about 1 x 7.5 cm) with an equal volume of a 25-percent solution of chromic acid. A piece of test paper, moistened with water, is placed on the top of the tube, which is then heated in a water bath for 5 minutes.

When the method was employed in this laboratory, however, no consistent results could be obtained. A large number of tests were consequently made in which all of the conditions were varied, singly and in combination. Test papers

had been allowed to dry and remoistened water were unreliable. It was found necessary to dip the filter paper into the dye solution diately before use. Further, conditions of test had to be redetermined each day when were begun, in order to obtain satisfactory lts.

o estimate small amounts of bromide, condi- were adjusted until a barely discernible pink was produced by 0.001 mole percent, and a y bright pink by 0.005. These conditions d within wide limits. For example, the time eating necessary to produce satisfactory colors day to day varied from 1½ to 15 minutes, and concentration of the chromic acid solution had e varied from 25 percent to a saturated solu- . The dye solution was sometimes used as pared, and sometimes had to be diluted as h as eightfold to obtain the desired color. se changes appeared to be made necessary by nges in the fluorescein solution effected by cipitation of fluorescein and by evaporation he solvent. Even the freshly prepared dye tions appeared to differ somewhat, possibly use of slight differences in the proportion of hol to water and in the temperature at which solution was saturated.

y replacing fluorescein with its sodium salt, nine, the most time-consuming steps of this cedure were eliminated. As the salt is readily ble in water, preparation of the dye solution considerably simplified. It was necessary to dissolve sufficient uranine in water to e a solution containing approximately 0.05 cent of the salt by weight. Solutions stored the laboratory for a month gave satisfactory lts. The stability of the dye solution made daily adjustment of test conditions unnecesy, and it was then possible to establish a defie procedure that yielded consistent results.

The modified procedure for the bromide test s as follows: Two-tenths milliliter of saturated omic acid solution was added to an equal vole of a saturated solution of the salt to be tested. circular piece of filter paper was dipped into the uranine solution and placed over the mouth of the test tube. A rack constructed of copper sheet and No. 10 copper wire, shown in figure 1, was found convenient for making several tests simultaneously. The rack holds six tubes and fits into a 250-ml beaker. The tubes were heated in boiling water for 6 minutes. Comparison solutions containing known amounts of bromide should be included with each set of unknown solutions tested. For very small amounts of bromide, when visual comparison is difficult, colors of the test papers can often be compared to advantage under ultraviolet light. One-thousandth mole percent can be detected, and the test is accurate to about ±0.002 mole percent.

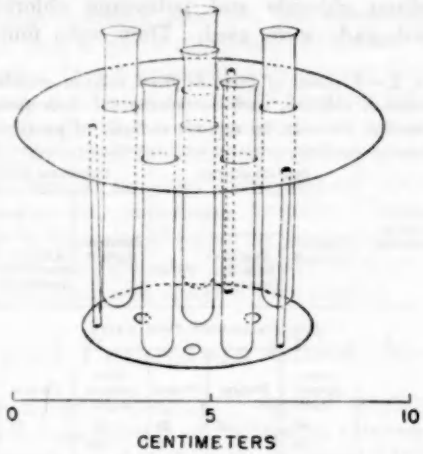


FIGURE 1.—*Copper rack used for supporting small test tubes in boiling water for the bromide test.*

This test can be adapted to the determination of larger amounts of bromide by increasing the concentration of the dye solution, decreasing that of the chromic acid solution, decreasing the time, or by diluting the solution to be tested. The last procedure is the most accurate. Because many organic materials, if present in sufficient amount, may react explosively with chromic acid, it is advisable to perform the test on the semimicroscale as described above.

# III. Methods of Purifying Sodium Chloride and Potassium Chloride

Four methods commonly used in purifying sodium and potassium chlorides for electrochemical work, namely, recrystallization from water, precipitation with ethyl alcohol [1, 10], precipitation with hydrogen chloride gas [11], and treatment with chlorine [12], were investigated to determine which was the most effective for removing bromide and for obtaining a satisfactory yield. On the basis of these results, a combination of methods was selected to prepare, in satisfactory yield, sodium and potassium chlorides free from bromide and other impurities.

Sodium chloride and potassium chloride of reagent-grade were used. They were found to contain initially 0.001 and 0.05 mole percent bromide, respectively. Sufficient potassium bromide was added to the filtered solution of each to be purified to make the bromide content 0.1 mole percent. Pyrex-glass vessels were used in all of the tests except the fusions. The bromide content of the products and the yields obtained by the different methods are shown in table 2.

TABLE 2.—*Removal of bromide from sodium chloride and potassium chloride, each containing 0.1 mole percent of potassium bromide, by various methods of purification*

| Number of successive treatments | Sodium chloride | | | Potassium chloride | | |
|---|---|---|---|---|---|---|
| | Bromide content | Yield | | Bromide content | Yield | |
| | | Average from one treatment | Total | | Average from one treatment | Total |
| **RECRYSTALLIZATION FROM WATER** | | | | | | |
| | *Mole percent* | *Percent* | *Percent* | *Mole percent* | *Percent* | *Percent* |
| 1 | 0.01 | 45 | 20 | * 0.05 | 35 | ------ |
| 2 | .003 | | 9 | .01 | | ------ |
| 3 | .003 | | | .005 | | 1.5 |
| **PRECIPITATION WITH ALCOHOL** | | | | | | |
| 1 | 0.01 | 30 | ------ | 0.01 | 45 | ------ |
| 2 | .003 | | 10 | .003 | | 20 |
| 3 | .003 | | 3 | .002 | | 9 |
| **PRECIPITATION WITH HCl** | | | | | | |
| 1 | 0.005 | 85 | ------ | 0.01 | 60 | ------ |
| 2 | .003 | | 75 | .003 | | 35 |
| 3 | .001 | | 65 | .001 | | 20 |
| **TREATMENT WITH $Cl_2$, CRYSTALLIZATION FROM WATER** | | | | | | |
| 1 | ---------- | ---------- | ---------- | 0.005 | 25 | ------ |
| 2 | ---------- | ---------- | ---------- | .002 | | 6 |
| **TREATMENT WITH $Cl_2$, PRECIPITATION WITH HCl** | | | | | | |
| 1 | 0.001 | 85 | 85 | 0.001 | 60 | 60 |

* Approximate figure.

## 1. Recrystallization From Water

Potassium chloride was recrystallized [illegible] times from water. In the first crystallization the following three fractions were taken: One by cooling the saturated solution from 100° to 25° C, a second by cooling from 25° to 6° C, and a third by evaporating the filtrate to about six-tenths of its volume and cooling to 6° C. The products represented 25, 13, and 27 percent, respectively, of the original material. All three contained rather large amounts of bromide, in excess of 0.01 mole percent. The first contained less than the second, and the second less than the third. The second and third fractions were discarded. In the subsequent recrystallizations a single fraction was taken by cooling the saturated solution to 25° C. Sodium chloride was recrystallized three times by evaporating a solution saturated at the boiling temperature to six-tenths of its volume and cooling to 6° C.

## 2. Precipitation With Ethyl Alcohol

Potassium chloride was purified by three successive precipitations from a saturated aqueous solution at room temperature by the addition of an equal volume of ethyl alcohol. By adding the saturated salt solution dropwise to the alcohol with stirring, the yield from each precipitation was increased from 35 to 45 percent. Sodium chloride was also purified by this latter procedure.

## 3. Precipitation With Hydrogen Chloride

Hydrogen chloride gas, generated by dropping concentrated hydrochloric acid into concentrated sulfuric acid, was passed into saturated solutions of sodium and potassium chlorides through an inverted glass funnel. The precipitated salt [illegible]

ed on a sintered glass filter, washed with portions of water, and dried at 110° C. successive precipitations were made. When idified solution of the product was tested by on of barium chloride solution, no sulfate etected.

### 4. Treatment With Chlorine

lorine was passed into a saturated solution of sium chloride for about 10 minutes. The solution was boiled to remove chlorine and bromine and brought to saturation at the boiling temperature. The salt was recrystallized by cooling the solution to 25° C, and a second recrystallization from water was made. The pH of the solution saturated with chlorine was found by glass-electrode measurement to be 2.2. An acidified sample of the purified salt was tested by the addition of potassium iodide and starch solution, and the mixture remained colorless.

## IV. Detection and Removal of Iodide

though iodide is not commonly found in re-grade chlorides in appreciable amounts, it thought desirable to determine whether e, if present, would be removed by the od found most satisfactory for the removal of ide. The test used for bromide was not table to the detection of iodide, probably be- of the lower volatility of iodine. Although e substitutes in fluorescein to form coral-pink rosin, the test did not appear to be suffi- ly sensitive. One-tenth mole percent was ired to produce a color on fluorescein paper, almost 1 mole percent was needed when ine was used. The salts were tested for iodide [13] by acidifying 6 ml of the saturated solution with 10 drops of 5-*M* hydrochloric acid, oxidizing the iodide, if present, with 2 drops of 3-percent hydrogen peroxide, and extracting the iodine with 6 ml of chloroform or carbon tetrachloride. One-thousandth mole percent of iodide produces a pale but discernible lavender color.

One-hundredth mole percent of potassium iodide was added to saturated solutions of sodium and potassium chlorides which also contained 0.1 mole percent potassium bromide. Tests for iodide in the salts obtained by precipitation with hydrogen chloride after treatment of their saturated solutions with chlorine were negative.

## V. Fusion of Sodium Chloride and Potassium Chloride

he most satisfactory means of removing hydro- ic acid from sodium or potassium chloride ipitated in a strong solution of the acid is to the salt to fusion. The fused salt is not only of occluded acid but is completely dry, a con- on often difficult to achieve at temperatures w the melting point [14]. Unfortunately, this tment usually yields a slightly alkaline pro- t. The total alkalinity amounted in several eriments to 0.001 to 0.01 mole per 100 moles of . Sodium chloride is normally considerably e alkaline after fusion than potassium chloride ted similarly.

ohnson [15] concluded that the alkali is formed a reaction of the vapor of the chloride with ospheric moisture. He found that the alka- y of sodium chloride could be reduced to 01 mole percent by drying the salt at 180° C fusing in an atmosphere of dry nitrogen. [16] showed that sodium chloride and potas- m chloride become alkaline when heated at ° C, or considerably below their melting points. Bjerrum and Unmack [17] titrated solutions of fused sodium chloride and potassium chloride with acid and found that the salts contained 0.003 and 0.001 mole percent, respectively, of free alkali. When Johnson fused sodium chloride in moist air, a product containing 0.005 mole percent of sodium hydroxide was obtained. On the contrary, Richards and Wells [18] state, "The salt remained strictly neutral after fusion in a vacuum, as it did in air." Because Richards and Wells fused samples of dry salt in an apparatus from which moisture would have been expelled during the early stages of heating, this observation is not at variance with the findings of Johnson.

The molten chlorides wet the surfaces of platinum boats and crucibles and adhere to the vessels on solidifying. Consequently, it is necessary to pour the fused salt into another platinum container whose temperature is sufficiently low so that the salt does not stick tightly. Protecting the hot salt from moist air under these conditions is obviously difficult.

The arrangement shown in figure 2 was found to be quite effective in reducing the hydrolysis of sodium and potassium chlorides during fusion. The 40-ml platinum crucible, *B*, fits loosely into the clear quartz tube, *A*, which is 11 cm long and 43 mm in diameter. Platinum foil, 0.005 in. thick, was used to form the trough, *C*. The foil was cut and folded to form the dam at the upper end. The Pyrex cover, *D*, fits snugly over the quartz tube but is loose enough to permit the dry nitrogen or air entering at the top to escape. Asbestos paper was wrapped around the quartz tube to permit the apparatus to be supported easily in the top of a crucible furnace with an opening 5 cm in diameter.

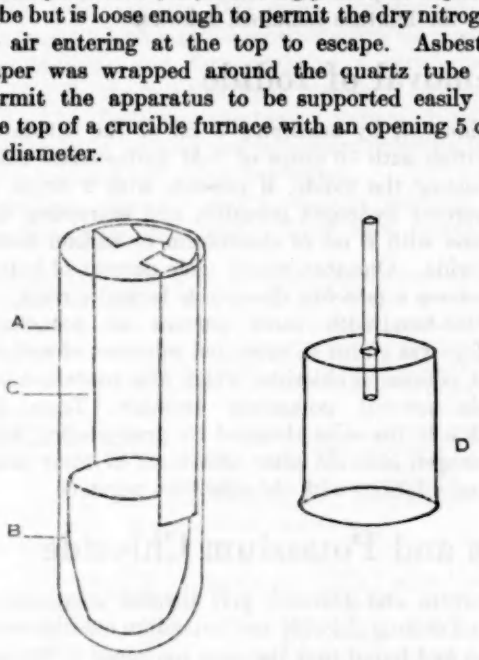


FIGURE 2.—*Apparatus for diminishing hydrolysis of sodium and potassium chlorides during fusion.*

*A*, Clear quartz tube; *B*, platinum crucible; *C*, platinum trough; *D*, glass cover.

The crucible was charged with about 20 salt that had been ground in an agate m and dried at 180° C. The cover was wi place, a slow stream of dry nitrogen pass 5 minutes to replace all of the moisture- air, and the tube finally supported in the t the furnace maintained at 1,000° C. The was usually completely melted in 10 to 15 min When all the salt had fused, the tube was drawn from the furnace, tipped to allow molten salt to flow into the cooler trough, placed on its side to cool with the nitrogen flowing.

By this procedure, neutral sodium and potas chlorides can be fused without introducing than 0.001 mole percent of free alkali. Ind sodium chloride dried at 180° C could usuall fused in this apparatus without the use of nitrogen, with satisfactory results. It app that moisture was expelled from the tube be fusion took place and did not enter again u the melt had solidified and partially coo Because its tendency toward hydrolysis at vated temperatures is less marked than tha sodium chloride, the potassium salt will usu contain after fusion no more than 0.003 m percent of free alkali, even though it be fuse an open crucible exposed to atmospheric moist When the apparatus shown in figure 2 is u however, the salts are nearly neutral.

The alkalinity of the chlorides was determi by titrating 5- to 12-g samples of fused salt wi 0.01-*M* solution of hydrochloric acid. Bro thymol blue was used as the indicator, and endpoint was established by comparison wit color standard prepared from the indicator an phosphate buffer of pH 7 [19].

# VI. Recommended Procedures

For use in precise electrometric work with the calomel or silver–silver-chloride electrodes, sodium chloride and potassium chloride should not contain more than 0.005 mole percent of bromide. If the accuracy of the measurement is expected to approach 0.02 mv, the quantity of bromide must be no greater than 0.002 mole percent. If, further, the salts are to be employed in pH work in conjunction with electrodes reversible to hydrogen (or hydroxyl) ion, the neutrality of the salt must be assured. It is likewise necessary that the procedure for drying the salt shall yield a prod that is known to be moisture free.

The requirements of electrometric pH work a therefore, somewhat different from those of oth types of physicochemical investigations. In pu fication procedures, the emphasis must be plac upon achieving a neutral salt free from bromi Other inert impurities need receive only seconda consideration.

Precipitation with hydrogen chloride was fou by Richards and Wells [18] to be the best meth

purifying sodium chloride. A commerical paration of the salt subjected to three precipi- ons gave a product with the same combining ght as other samples prepared by several other e elaborate procedures. As shown in the ceding sections, about 98 percent of the bro- e can be removed from a saturated solution of um chloride by a single treatment with rine and one precipitation with hydrogen ride. It can be concluded from the work of hards and Wells that two successive precipita- s would reduce the amounts of other impurities he negligible level. They also found that the did not pick up moisture during weighing in winter air. The fused salt can, however, be tured and weighed in large lumps to minimize tendency to adsorb moisture from humid nospheres.

The treatment with chlorine and precipitation h hydrogen chloride is apparently effective for oving bromide and iodide from potassium oride, as well as from the sodium salt. The estigation described by Richards [20] is un- btedly the most detailed and most carefully cuted study of the removal of the other urities from the salt. In order to remove stances isomorphous with potassium chloride, hards subjected commercial potassium nitrate repeated recrystallization. The nitrate was then converted to chloride which was, in turn, further purified by precipitation with hydrogen chloride. As the elimination of small amounts of other alkali halides from sodium chloride was readily effected by precipitation with hydrogen chloride [18], it seems reasonable to assume that they would be similarly removed from potassium chloride. Other isomorphous impurities normally are present in extremely small amounts.

In the light of these considerations, it can be concluded that the same procedure will serve to prepare sodium chloride and potassium chloride with less than 0.002 mole percent of bromide and free of iodide and significant amounts of inert impurities.

Chlorine is bubbled for 10 minutes at a moderate rate through a filtered solution of the salt, saturated at room temperature. The solution is then boiled for 5 minutes to remove free halogens. The salt is precipitated twice with hydrogen chloride from a solution saturated at room temperature, collected on a filter, preferably of sintered glass, washed with small portions of pure water, and dried at 180° C. Finally, the salt is fused, as described in the previous section, to remove occluded water and hydrochloric acid. These preparations should meet the most exacting requirements of electrochemical work.

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# Preparation of Mannuronic Lactone From Algin

*By Harriet L. Frush and Horace S. Isbell*

A simple procedure is reported for the preparation of crystalline mannuronic lactone from algin. The algin is converted to alginic acid, which is hydrolyzed by the action of concentrated sulfuric acid followed by dilute acid. In contrast to prior methods, the lactone is crystallized directly from the hydrolyzate of alginic acid without the intermediate separation of the amorphous barium salt or the cinchonine salt. The yield is from 25 to 30 percent of the alginic acid used. The preparation and properties of crystalline sodium mannuronate and potassium mannuronate monohydrate are also described.

## I. Introduction

Mannuronic acid, one of the three naturally urring uronic acids, is of particular interest ause it plays an important role in the structure many marine plants, and is the chief constituent algin, a product of growing commercial impor- ce. It has been prepared by others in the form he crystalline lactone [1, 2] [1] and two modifica- ns of the free acid [3]. It may be separated st readily as the lactone, but prior methods of paration are so unsatisfactory that it has been ated only in small quantities. To make the stance more available for study and research, simple procedure has been developed for the paration of mannuronic lactone directly from hydrolyzates of alginic acid. Inasmuch as raw materials used are commercially available relatively low cost, the preparation of man- ronic lactone in any desired quantity now be- mes practicable.

Crystalline mannuronic lactone was first pre- ared by Nelson and Cretcher [1] by the acid drolysis of alginic acid, followed by the inter- ediate preparation of amorphous barium man- uronate and crystalline cinchonine mannuronate. The method is laborious and the yield is very w. Schoeffel and Link [2] separated mannu- nic lactone from the hydrolyzate of alginic acid means of a carefully purified amorphous rium salt without recourse to the cinchonine salt. Fractional precipitation of the unhydrolyzed polymannuronates and various clarifications, filtrations, and concentrations were required to give the crystalline lactone in yields calculated to be 8.3 percent of the theoretical (based on the uronic acid content of the alginic acid). In both methods the hydrolyzates were neutralized by prolonged heating with barium carbonate.[2] This treatment is necessary for complete neutralization, but it causes considerable decomposition of the mannuronic acid.

In the foregoing procedures it was necessary to prepare and purify one or even two intermediate compounds because it was impossible to crystallize mannuronic lactone directly from the crude

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] Nelson and Cretcher neutralized the hot hydrolyzate with barium carbonate, but later changed the procedure to include partial neutralization with barium hydroxide at room temperature followed by treatment with barium carbonate for 2 hours at boiling temperature.

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hydrolyzate. Apparently the difficulty in crystallizing mannuronic lactone arises, first, from incomplete hydrolysis of the polysaccharide, and second, from decomposition reactions incident to the high-temperature neutralization of the hydrolyzate with barium carbonate. The hydrolysis is complicated by the fact that alginic acid is only slowly cleaved by hot acids, whereas under the conditions of the reaction, the product, mannuronic acid, is partially decomposed with the formation of carbon dioxide and furfural. Nelson and Cretcher found that on boiling for 18 hours with distilled water, alginic acid loses 10 percent of the theoretical amount of carbon dioxide; on boiling for 5 hours with 12-percent hydrochloric acid it loses 86 percent of the theoretical amount. To avoid the undesirable decomposition reaction, they recommended hydrolysis with 80-percent sulfuric acid at room temperature for 5 days. Schoeffel and Link, however, hydrolyzed by boiling with 2.5-percent sulfuric acid for 15 hours.

Thus, it seemed probable that if a more complete hydrolysis of algin were effected, and the neutralization of the hydrolyzate were avoide might be possible to crystallize mannuronic lac directly from the hydrolyzate. With this o in view, various methods were tried for hydrol alginic acid and for neutralizing the hydrol The experiments led to a simple procedure fo hydrolysis, followed by removal of the sul acid at room temperature, without conversi the mannuronic acid to a salt. After concen tion of the hydrolyzate, crystalline mannu lactone separates in yields of 25 to 30 percen the uronic acid content of the alginic acid.

In the course of the investigation, the possibi of separating mannuronic acid as a crystal salt was considered, and attempts were mad find a suitable substance. Crystalline sod mannuronate and potassium mannuronate w prepared, and their properties are reported h The salts crystallize readily but are too sol for use in the preparation of mannuronic lacto

# II. Experimental Details

## 1. Preparation of Alginic Acid

Alginic acid is an intermediate in the industrial preparation of algin, but at present it is not commercially available. It may be readily prepared from commercial algin by the following procedure: 1 kg of algin is stirred for 2 hours with a solution consisting of 3 liters of alcohol,[3] 2 liters of water, and 350 ml of concentrated hydrochloric acid. The crude alginic acid is then separated by vacuum filtration in a large Büchner funnel, or more conveniently in an 8-liter conical percolator equipped with a perforated plate and a cheesecloth filter pad. It is then stirred with a solution containing 1 liter of alcohol, 3 liters of water, and 100 ml of concentrated hydrochloric acid. After 2 hours the alginic acid is again separated by vacuum filtration, and during a period of several days is washed by gravity in the funnel or percolator with a large volume of water. When the wash water is free from chlorides, the material is washed with alcohol and then dried in air and finally in a vacuum at 60° C. The yield of alginic acid is approximately 700 g. When a product prepared by the above method was boiled for 8 hours with 18-percent hydrochloric acid, it gave car dioxide equivalent to 90 percent of mannur anhydride.

[3] Methyl, ethyl, or isopropyl alcohol may be used.

## 2. Preparation of Mannuronic Lacto From Alginic Acid

Eighty grams of alginic acid is added qui to 100 ml of ice-cold, concentrated sulfuric ac The pasty mass is kept in an ice bath and is stir constantly with a heavy glass rod for 10 minu It is stored in a refrigerator for 18 hours and th is thoroughly mixed with 8 liters of water. T diluted mixture is boiled under reflux for hours,[5] cooled to room temperature, and treat with a quantity of calcium carbonate equivalent the sulfuric acid. The pH of the resulting so tion should be 2.3. If not, the acidity is a justed by the addition of either calcium carbon or dilute sulfuric acid.

[4] When alginic acid is mixed with concentrated sulfuric acid, the pro turns straw-colored, then brown, and finally black. The dark mixture, w diluted with acetic anhydride, appears deep blue; with acetic acid, red violet; and with water or alcohol, yellowish-brown. Apparently the d color originally formed is not caused by carbonization, but arises fro highly-colored substance.

[5] A Glas-col mantle provides a convenient source of heat without dan of overheating the material. Boiling chips should be used to prevent bu ing.

FIGURE 1.—*A, Sodium mannuronate; B, potassium mannuronate monohydrate*

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e mixture is filtered with the aid of decolor- carbon, and the residue on the filter is ed and discarded. The filtrate is evaporated ° C or less under reduced pressure to a vol- of about 400 ml. The calcium sulfate that tallizes during the evaporation is separated, ed with hot water until free from reducing tances, and discarded. The solution and hings are combined and evaporated under ced pressure to a volume of about 100 ml. his point the calcium sulfate is again separated, ed, and discarded, and the solution is evap- ed under reduced pressure to a thick sirup ut 40 ml). Ordinarily, mannuronic lactone ns to crystallize during the final evaporation. sirup is diluted with approximately 2 vol- s of acetic acid, seeded (if crystallization has already started), and allowed to stand in the gerator for 18 hours.[6] The crystals are then rated by filtration and washed, first with a ture consisting of 3 parts of acetic acid and 1 of water, and finally with acetone.[7] The duct contains a small quantity of calcium ate, which is removed by dissolving the lactone in hot water and filtering the solution with the aid of a decolorizing carbon. The lactone crystallizes almost quantitatively when the solution is evaporated in vacuum or in a stream of dry air.

In numerous preparations by the above method in which the alginic acid used had a mannuronic anhydride content of 90 percent, the main crop of crystals weighed between 20 and 24 g and contained less than 1 g of calcium sulfate. In a typical preparation, the crude lactone from 80 g of alginic acid weighed 21.2 g, contained 0.36 g of calcium sulfate, and had a specific rotation of +87.2° (30 minutes after dissolution in water). After recrystallization from water, the product weighed 20.1 g. $[\alpha]_D^{20}=+92.0°$ (30 minutes), whereas for pure mannuronic lactone, $[\alpha]_D^{20}=$ 92.2° (30 minutes) [4]. The yield of the recrystallized lactone was 25.1 percent of the weight of the alginic acid, or 27.9 percent of the theoretical.

[6] Nearly as satisfactory results can be obtained by the addition of a suitable quantity of either acetone or dioxane. As crude sirups of mannuronic lactone gradually darken and decompose, they should be kept at a low temperature.

[7] A small, rather crude second crop may sometimes be obtained by concentration of the mother liquor and subsequent dilution with acetic acid.

# III. New Crystalline Salts of Mannuronic Acid

## 1. Sodium Mannuronate

Twenty grams of mannuronic lactone was dis- ved in water at room temperature and slightly than the theoretical amount of sodium bi- bonate (10.5 g) was added in portions with ring. The solution was filtered with the aid a decolorizing carbon, and concentrated under uced pressure to a volume of about 35 ml. fficient ethyl alcohol was added to cause a faint bidity that was discharged by the addition a drop of water. The solution was seeded and owed to crystallize while in motion. Alcohol s added from time to time as crystallization ceeded until the volume of the mixture was 0 ml. After 2 days the crystals of sodium man- ronate were collected on a filter, washed with ueous ethyl alcohol, and finally with 95-percent ohol. They were dried in a vacuum at room mperature over calcium chloride. The yield of ude, yellow-colored sodium mannuronate was .0 g. After two successive recrystallizations by solving the crystals in water at room tempera- re and treating the solution in the manner de- ribed above, the compound was obtained as a hite crystalline powder composed of slender prisms (fig. 1). Further recrystallization produced no change in optical rotation.

*Analysis:* Calculated for $C_6H_9O_7Na$: C, 33.33; H, 4.20. Found: C, 33.4; H, 4.3.

When dissolved in water containing carbon dioxide, the compound exhibits a small mutarotation (table 1), which at 20° C is substantially complete in 2 minutes. $[\alpha]_D^{20}=-6.6°$ (water, c=4) (30 minutes).

TABLE 1.—*Mutarotation of sodium mannuronate in water saturated with carbon dioxide*

| 2 g per 100 ml of solution at 20° C read in a 2-dm tube | | |
|---|---|---|
| Time | Observed reading | $[\alpha]_D^{20}$ |
| *Minutes* | ° *S* | |
| 0.5 | −1.65 | −14.3 |
| .7 | −1.35 | −11.7 |
| .9 | −1.17 | −10.1 |
| 1.0 | −0.97 | −8.4 |
| 1.5 | −.80 | −6.9 |
| 1.8 | −.79 | −6.8 |
| 2.1 | −.76 | −6.6 |
| 2.4 | −.77 | −6.7 |
| 2.8 | −.75 | −6.5 |
| 3.1 | −.82 | −7.1 |
| 5.0 | −.76 (constant) | −6.6 |

## 2. Potassium Mannuronate Monohydrate

Twenty grams of mannuronic lactone were dissolved at room temperature in water saturated with carbon dioxide, and the solution was treated with 11.2 g of potassium bicarbonate. Potassium mannuronate monohydrate was then crystallized in the manner dsecribed for sodium mannuronate. The crude material (16 g) was recrystallized twice from water and alcohol. The optical rotation of the substance was not altered by further recrystallization from water alone.

*Analysis:* Calculated for $C_6H_9O_7KH_2O$: C, 28.80; H, 4.43. Found: C, 29.1; H, 4.6.

The crude potassium mannuronate had a yellow color, but the pure compound was obtained in long, colorless plates or prisms (fig. 1). Like sodium mannuronate, it exhibits a rapid mutarotation, which is complete in less than 3 min (table 2). $[\alpha]_D^{20} = -5.6°$ (water, $c=4$) (30 min

TABLE 2.—*Mutarotation of potassium mannuronate hydrate in water saturated with carbon dioxide*

| 2 g per 100 ml of solution at 20° C read in a 2-dm tube | | |
|---|---|---|
| Time | Observed reading | $[\alpha]_D^{20}$ |
| *Minutes* | ° *S* | |
| 0.5 | −2.12 | −18.3 |
| .7 | −1.83 | −15.8 |
| .9 | −1.68 | −14.5 |
| 1.0 | −1.40 | −12.1 |
| 1.3 | −1.07 | −9.3 |
| 1.8 | −0.91 | −7.9 |
| 2.0 | −.82 | −7.1 |
| 2.4 | −.75 | −6.5 |
| 2.9 | −.69 | −6.0 |
| 5.0 | −.65 (constant) | −5.6 |

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